VOL. VII. [JANUARY, 1886.] NO. 6.

AMERICAN CHEMICAL JOURNAL.

ON BENZOYLACETIC ACID AND SOME OF ITS DERIVATIVES. PART III.[1]

BY W. H. PERKIN, Jun., *Privatdocent at the University of Munich.*

In the first two parts of this research I described a number of simpler derivatives of ethylic benzoylacetate, showing it to be analogous to ethylic acetoacetate in almost every respect. In the third part I wish to give an account of some of the more complicated reactions into which this body enters, namely, the preparation and properties of ethylic dibenzoylsuccinate, ethylic monobenzoylsuccinate, and dehydrobenzoylacetic acid.

Ethylic Dibenzoylsuccinate.

By the action of iodine on the sodium compound of ethylic acetoacetate, Harrow[2] obtained ethylic diacetylsuccinate, according to the equation:

$$\begin{matrix}CH_3.CO.CHNa.COOEt\\CH_3.CO.CHNa.COOEt\end{matrix} + I_2 = \begin{matrix}CH_3.CO.CH.COOEt\\CH_3.CO.CH.COOEt\end{matrix} + 2NaI.$$

On boiling this compound with dilute sulphuric acid it is partly hydrolysed, giving off one molecule of alcohol, and forming the ethylic salt of carbopyrotritaric acid, thus:

$$C_{12}H_{18}O_6 = C_{10}H_{12}O_5 + C_2H_5.OH.$$

If the saponifying action is continued further, this ethereal salt is split up into carbopyrotritaric acid and alcohol:

$$C_{10}H_{12}O_5 + H_2O = C_8H_8O_5 + C_2H_5.OH.$$

[1] Communicated by the Author.

[2] Trans. 1878, 425.

This acid, which Harrow supposes to have the constitution:

$$\begin{matrix}CH_3.CO\\COOH\end{matrix}\!\!>\!CH.CH\!<\!\!\begin{matrix}C(CH)\\CO\end{matrix}\!\!>\!O,$$

is resolved, on further heating with dilute sulphuric acid, into pyrotritaric acid and carbonic anhydride, thus:

$$C_8H_8O_5 = C_7H_8O_3 + CO_2.$$

On account of this latter reaction, Harrow assigns the following constitution to pyrotritaric acid:

$$CH_3.CO.CH(COOH).CH:C:CH_2.$$

Considering the complicated nature of these reactions, it appeared to be interesting to repeat them with ethylic benzoylacetate, in order to determine whether similar compounds would be produced, corresponding with carbopyrotritaric and pyrotritaric acids.

It was necessary, in the first place, to prepare ethylic dibenzoylsuccinate, which can easily be effected by a method analogous to that employed by Harrow for preparing ethylic diacetylsuccinate, namely, by the action of iodine on ethylic benzoylsodacetate. 4.7 grams of the finely powdered sodium compound were mixed with dry ether, and 2.8 grams of iodine added in small quantities at a time, the whole being well shaken and cooled after each addition. At first the color of the iodine disappears instantly, but towards the end of the reaction much more slowly, the mixture becoming slightly brownish.

The ethereal solution is filtered from the precipitated sodic iodide, washed with water and a little sulphurous acid in order to remove any slight excess of iodine, and then dried over calcium chloride. On distilling off the ether, a brownish mass remains, which becomes almost entirely solid when exposed for about 24 hours over sulphuric acid in a vacuum. These crystals are spread out on a porous plate, in order to remove as much of the mother-liquor as possible, washed on a filter, with small quantities of ether, until an almost colorless mass remains behind, and purified by two crystallisations from alcohol.

0.1630 gram substance gave 0.0890 gram H_2O and 0.4113 CO_2.

	Found.	Theory, $C_{22}H_{22}O_4$.
C	68.82 per cent.	69.11 per cent.
H	6.06	5.76
O	25.12	25.13

The compound is therefore ethylic dibenzoylsuccinate, formed according to the equation:

$$\begin{matrix} C_6H_5.CO.CHNa.COOEt \\ C_6H_5.CO.CHNa.COOEt \end{matrix} + I_2 = \begin{matrix} C_6H_5.CO.CH.COOEt \\ | \\ C_6H_5.CO.CH.COOEt \end{matrix} + 2NaI.$$

Ethylic dibenzoylsuccinate melts at 128–130°, and when heated in a test tube it is decomposed, a carbonaceous residue being left. It is sparingly soluble in cold alcohol, but easily in hot, being deposited from this solution on cooling in short thick prisms; it may be obtained perfectly colorless by repeated recrystallisation. It is easily soluble in ether and benzene, crystallising in small needles on evaporation.

The behavior of ethylic dibenzoylsuccinate with concentrated sulphuric acid is very characteristic. The finely powdered substance dissolves in the acid, forming an almost colorless solution, and on adding water is reprecipitated, apparently unchanged. When the solution is heated it becomes first reddish and then olive-green, but if the heating is continued the color changes to a bluish-red. If this solution when cold is poured into a little water, a brownish liquid is obtained, with a strong blue fluorescence; an excess of water destroys the coloration altogether. As ethylic benzoylsuccinate contains two CH groups which are each joined on both sides to carbonyl groups, it appeared very probable that it might yield a disodium compound on treatment with sodium ethoxide, according to the equation:

$$\begin{matrix} C_6H_5.CO.CH.COOEt \\ | \\ C_6H_5.CO.CH.COOEt \end{matrix} + 2NaOEt = \begin{matrix} C_6H_5.CO.CNa.COOEt \\ | \\ C_6H_5.CO.CNa.COOEt \end{matrix} + 2EtOH.$$

This was in reality found to be the case, the compound being best formed in the following way: 0.3 gram of sodium is dissolved in the smallest possible quantity of alcohol, and while still warm an excess of pure dry ether is added, the whole being thoroughly mixed, by means of a glass rod, until the liquid becomes clear, or only slightly turbid. An ethereal solution of 2.5 grams of ethylic dibenzoylsuccinate is then added, and the whole allowed to stand for some time. The sodium compound slowly separates out as a slightly yellowish mass, and as soon as the precipitation is finished

it is collected by means of a vacuum pump, and well washed, first with a mixture of alcohol and ether, and lastly with ether, in which the compound is almost insoluble. The disodium compound was thus obtained as an almost colorless mass, which, after standing for some hours over sulphuric acid in a vacuum, gave the following numbers on analysis:

0.4434 gram substance gave 0.1575 Na_2SO_4.

	Found.	Theory.
Na	11.49 per cent.	10.80 per cent.

When perfectly dry this compound is fairly stable, but if it contains a little alcohol it quickly takes up moisture from the air and is decomposed. It is fairly soluble in hot alcohol, sparingly in the cold. On adding a drop of ferric chloride to the alcoholic solution, a dirty red coloration is formed. Cupric acetate precipitates the copper salt as a light-green amorphous mass. The sodium compound is easily decomposed by dilute acids, the original substance being apparantly regenerated.

If this compound is treated with an ethereal solution of iodine, sodium iodide is instantly precipitated, and on filtering and evaporating the ethereal solution a thick brownish oil is obtained, which is probably ethylic dibenzoylfumarate, produced according to the equation:

$$\begin{matrix} C_6H_5.CO.CNa.COOEt \\ C_6H_5.CO.CNa.COOEt \end{matrix} + I_2 = \begin{matrix} C_6H_5.CO.C.COOEt \\ \| \\ C_6H_5.CO.C.COOEt \end{matrix} + 2NaI.$$

The oil, unfortunately, would not crystallise, and therefore a good analysis could not be obtained. The solution in chloroform, however, decolorised bromine instantly, without evolution of hydrobromic acid, showing that it is an unsaturated compound.

Decomposition Products of Ethylic Dibenzoylsuccinate.

On mixing ethylic dibenzoylsuccinate with alcoholic potash it dissolves, producing an intense yellow solution. If after allowing it to remain for some time, or gently warming, the product be acidulated with dilute sulphuric acid, a yellow amorphous acid is precipitated; unfortunately, however, this could not be obtained in a crystalline state, as it is extremely soluble in all solvents except water. In order to purify it as far as possible it was dissolved in ammonia, and fractionally precipitated with dilute acid;

this treatment having been repeated several times, the product was finally converted into the silver salt, and analysed with the following result:

0.3047 gram substance gave 0.1171 gram Ag.

	Found.	Theory, $Ag_2C_{18}H_{12}O_6$.
Ag	38.43 per cent.	40.00 per cent.

Although these numbers do not agree very closely with theory, it is yet probable that the substance is in reality impure dibenzoylsuccinic acid. On adding ferric chloride to the solution of the acid in alcohol, or that of the ammonium salt, a peculiar dark-green precipitate is formed, closely resembling that obtained with sulphuric acid.

The acid dissolves in concentrated sulphuric acid, producing a yellowish solution which becomes of a beautiful crimson on warming. The acid gives acetophenone when distilled with soda-lime. From the above experiments it appeared unlikely that better results would be obtained by saponifying with other alkalis, such as baryta-water, and it was thought probable that, as in the case of ethylic diacetylsuccinate, dilute acids might be employed with greater advantage. The following method of hydrolysis was finally adopted.

Pure ethylic dibenzoylsuccinate was boiled with an excess of dilute sulphuric acid (1 : 2) for about six hours in a flask connected with a reflux condenser, at the end of which a test-tube containing baryta-water was fixed. The mass became more and more darkly colored, but very little carbonic anhydride was given off. When cold, the product was collected, washed with water, well shaken with a warm solution of sodic carbonate, and filtered. The residual tarry mass was then washed with water, again boiled with dilute sulphuric acid for six hours, and the extraction with sodic carbonate repeated as before. The greater part dissolved, leaving a thick black residue, from which mere traces of an organic acid were obtained on repeating the treatment with sulphuric acid.

The different alkaline solutions were mixed and acidified with dilute sulphuric acid. This produced a precipitate which, after being recrystallised several times from dilute acetic acid (70 per cent.), was obtained pure in the form of small colorless needles which gave the following numbers on analysis:

I. 0.1862 gram substance gave 0.0664 H_2O and 0.4752 CO_2.

II. 0.2032 gram substance gave 0.0745 H_2O and 0.5249 CO_2.

III. 0.1627 gram substance gave 0.0592 H_2O and 0.4167 CO_2.

	Found.			Theory, $C_{18}H_{12}O_5$.
	I.	II.	III.	
C	69.60	70.42	69.85 per cent.	70.13 per cent.
H	3.96	4.07	4.04	3.89
O	26.44	25.51	26.11	25.97

The formula of this acid is therefore $C_{18}H_{12}O_5$, and it is formed from ethylic dibenzoylsuccinate by the removal of 2 mols. of alcohol, thus:

$$\underset{\text{Ethylic dibenzoyl-succinate.}}{C_{22}H_{22}O_6} + H_2O = \underset{\text{New acid.}}{C_{18}H_{12}O_5} + 2C_2H_5.OH,$$

its formation corresponding precisely with that of carbopyrotritaric acid from ethylic diacetylsuccinate:

$$C_{12}H_{18}O_6 + H_2O = C_8H_8O_5 + 2C_2H_5.OH.$$

This new acid melts at 236–238°. It is easily soluble in ether, alcohol, benzene, light petroleum, and glacial acetic acid, less so in a 70 per cent. solution of the latter solvent, from which it crystallises in small needles. The alcoholic solution gives an orange coloration with ferric chloride.

This acid, $C_{18}H_{12}O_5$, dissolves in concentrated sulphuric acid, forming a colorless solution, which, however, acquires a beautiful violet color when warmed. Heated by itself in a test-tube, it first melts and then sublimes, water being given off at the same time. The sublimate is crystalline, but apparently insoluble in ammonia, and is perhaps the anhydride of the acid. The acid $C_{18}H_{12}O_5$ is easily decomposed on distilling it with soda-lime, acetophenone being formed. Its alcoholic solution does not appear to react with phenylhydrazine or hydroxylamine. It is, however, a strong acid, dissolving easily in ammonia, sodic hydroxide, or sodic carbonate solutions. The ammonium salt was prepared by dissolving the acid in ammonia and then allowing the solution to stand over sulphuric acid in a vacuum until the excess of alkali had evaporated. On adding silver nitrate to this solution, a white precipitate of the silver salt was formed; this, when dried over sulphuric acid in a vacuum, gave the following numbers on analysis:

0.4817 gram substance gave 0.1939 gram silver.

		Theory.	
	Found.	$C_{18}H_{10}O_5Ag_2$.	$C_{18}H_{12}O_5Ag_2$.
Ag	40.25 per cent.	41.29 per cent.	40.00 per cent.

This result not being satisfactory, a complete analysis of the silver salt was made with the following result:

0.2683 gram substance gave 0.400 CO_2, 0.0562 H_2O and 0.1087 Ag.

	Found.	Theory. $C_{18}H_{16}O_5Ag_2$.	Theory. $C_{18}H_{12}O_4Ag_2$.
C	40.66 per cent.	41.44	40.00 per cent.
H	2.32	1.91	2.22
Ag	40.52	41.29	40.00
O	16.50	15.35	17.77

This silver salt is very stable, being only slowly discolored on standing in the air by daylight. The solution of the ammonium salt gives the following reactions: Barium chloride precipitates the *barium salt* as a white amorphous mass, insoluble in water, but slightly soluble in alcohol. The *calcium salt* is thrown down by calcium chloride as a heavy, white, amorphous powder insoluble in water. Dried at 100° and analysed, it gave the following result:

0.2625 gram substance gave 0.0949 gram $CaSO_4$.

	Found.	Theory. $C_{18}H_{16}O_5Ca$.	Theory. $C_{18}H_{12}O_4Ca$.
Ca	10.63 per cent.	11.56 per cent.	10.99 per cent.

The *copper salt* is precipitated on the addition of cupric sulphate as a light-green, almost colorless mass, which is very sparingly soluble in water. It dissolves in ammonia and sodic hydroxide solution with a blue color.

On boiling these solutions, the salt is decomposed, copper oxide being precipitated.

Ferric chloride produces a reddish-brown precipitate, very much resembling that produced in solutions of benzoic acid or its salts.

Ferrous sulphate gives no precipitate.

On adding a solution of acetate of lead, the *lead salt* is thrown down as a heavy white mass, almost insoluble in water.

If a solution of zinc sulphate be added to the ammonia salt, the whole remains clear for some time, but after standing the *zinc salt* slowly separates out as a white powder, which is somewhat soluble in hot water.

The *nickel salt* is formed on adding a solution of sulphate of

nickel as a light-green precipitate, which is soluble in ammonia, producing a beautiful blue solution.

Action of Acetic Anhydride on the Acid $C_{18}H_{12}O_5$.

In order to obtain some clue as to the constitution of this acid, several experiments were tried with different reagents, mostly without result. On heating it with acetic anhydride, however, it was found that the acid easily gave up the elements of water, being converted into an indifferent body, according to the equation—

$$C_{18}H_{12}O_5 = C_{18}H_{10}O_4 + H_2O.$$

In order to examine this new compound, the pure acid, $C_{18}H_{12}O_5$, was heated with an excess of acetic anhydride for about an hour in a flask connected with a reflux condenser. On cooling, the solution which had become slightly yellowish was diluted with water and allowed to remain until the excess of acetic anhydride had dissolved. During this operation a beautifully crystalline substance separated, which was collected, well washed with water, recrystallised once from acetic acid, and analysed, with the following result:

0.1961 gram substance gave 0.0670 gram H_2O and 0.5329 gram CO_2.

	Found.	Calculated, $C_{18}H_{10}O_4$.
C	74.11 per cent.	74.48 per cent.
H	3.79	3.45
O	22.10	22.07

It melts at 254–255° with slight decomposition. If heated carefully in a test-tube, the greater part sublimes, but considerable decomposition takes place, and a black residue is left. The sublimate is crystalline, and probably identical with that obtained by treating the acid $C_{18}H_{12}O_5$ in the same way. The compound $C_{18}H_{10}O_4$ is sparingly soluble in hot alcohol, yielding a solution with a most beautiful violet fluorescence very much like that exhibited by anthracene. It is nearly insoluble in cold alcohol. The solution in hot alcohol gives an orange coloration with ferric chloride. The substance crystallises beautifully from its solution in hot glacial acetic acid, which on cooling deposits it in glittering plates. It is easily soluble in hot benzene, and on adding light petroleum is precipitated in a beautifully crystalline condition. It

is easily soluble in chloroform, but only sparingly in ether or bisulphide of carbon. It dissolves in concentrated sulphuric acid, yielding a yellowish-green solution which changes to a violet color on warming.

The compound $C_{18}H_{10}O_4$ is neutral, being almost insoluble in ammonia and potash solution, and apparently quite insoluble in sodic carbonate solution.

Action of Potash on the Compound $C_{18}H_{10}O_4$.

If this substance is warmed with fairly concentrated alcoholic potash, it dissolves without becoming discolored or any apparent decomposition taking place. In order to further examine this reaction, the liquid was heated for ten minutes on a water-bath, and then diluted with water, when the whole dissolved, forming a slightly yellowish solution. On adding dilute sulphuric acid, a solid acid was precipitated, which was collected, well washed with water, dissolved in alcohol, and filtered; in this way a small quantity of unchanged $C_{18}H_{10}O_4$ was easily removed. On evaporation, the filtrate deposited a solid crystalline acid, which after recrystallising from dilute acetic acid was analysed with the following result:

0.1865 gram substance gave 0.0668 gram H_2O and 0.4758 gram CO_2.

	Found.	Calculated, $C_{18}H_{12}O_5$.
C	69.58 per cent.	70.13 per cent.
H	3.98	3.89
O	26.44	25.97

This substance was, therefore, the original acid, $C_{18}H_{12}O_5$, formed from the compound $C_{18}H_{10}O_4$ by the addition of water, according to the equation,

$$C_{18}H_{12}O_4 + H_2O = C_{18}H_{12}O_5.$$

It melted at 230–235°, and had all the properties of the acid obtained by the action of dilute sulphuric acid on ethylic dibenzoylsuccinate.

Constitution of the Acid $C_{18}H_{10}O_5$.

Harrow by the action of dilute sulphuric acid on ethylic diacetylsuccinate[1] obtained carbopyrotritaric acid, $C_8H_8O_5$, which from his

[1] Trans. 1878, 428.

analyses of its salts would seem to be a monobasic acid. When boiled with potash, however, it is converted into the potash salt of a bibasic acid, $C_8H_{10}O_6$, which gives salts of the formula $C_8H_8O_6M_2$.

The acid $C_{18}H_{18}O_8$ is, however, either bibasic or else very easily converted into a bibasic acid, as it gives directly salts containing two atoms of the metal; unfortunately, from the analyses it is not clear whether these have the formula $C_{18}H_{16}O_8M_2$ or $C_{18}H_{12}O_8M_2$. It is, however, possible that these acids, $C_{18}H_{18}O_8$ and $C_8H_8O_8$, are in reality anhydro-acids, the former acid when dissolved in ammonia or alkalis being converted into salts of an unstable acid, $C_{18}H_{14}O_8$.

Since the publication of an abstract of this research[1] the carbopyrotritaric acid has been more thoroughly examined by Knorr,[2] who considers it to be a bibasic acid forming salts of the formula $C_8H_6O_6Ag_2$. On account of the formation of ethylic carbopyrotritarate by the action of concentrated sulphuric acid on ethylic diacetylsuccinate in the cold, according to the equation,

$$C_{12}H_{18}O_6 - H_2O = C_{12}H_{16}O_5,$$

Knorr comes to the conclusion that carbopyrotritaric acid must have the following constitution:

$$\begin{matrix} COOH.C:C(CH_3) \\ | \\ COOH.C:C(CH_3) \end{matrix} > O,$$

it being, in fact, dimethylfurfuranedicarboxylic acid. Since the publication of Knorr's research I have tried the action of concentrated sulphuric acid on ethylic dibenzoylsuccinate, and found that it behaves in exactly the same way as the diacetylsuccinate, although, unfortunately, having very little material at my command, I have not been able to analyse the immediate product corresponding with the ethylic carbopyrotritarate.

Ethylic dibenzoylsuccinate dissolves easily in concentrated sulphuric acid, the mixture becoming slightly warm and brownish colored. If water be added to it after standing for 15 hours, an oil is precipitated which soon becomes solid. This was extracted with ether, and on allowing the solution to evaporate, a beautiful substance was obtained, crystallising in long thick prisms melting at 85°. This is undoubtedly the diethyl salt of the acid $C_{18}H_{18}O_8$,

[1] Ber. **17**, 59. [2] *Ibid.* **17**, 2863.

as on saponification with potash it gives the acid in a perfectly pure state, melting at 236–237°. In order to explain the formation of this acid, $C_{18}H_{12}O_5$, it is necessary in the first place to suppose the formula of ethylic dibenzoylsuccinate transformed into an isomeric unstable modification, thus:

$$\begin{array}{l}\mathrm{COO(C_2H_5).CH.CO.C_6H_5}\\ \mathrm{COO(C_2H_5).CH.CO.C_6H_5}\end{array} = \begin{array}{l}\mathrm{COO(C_2H_5).C:C(OH).C_6H_5}\\ \mathrm{COO(C_2H_5).C:C(OH).C_6H_5}\end{array}.$$

On treating this with sulphuric acid, water is eliminated, the diethyl salt of diphenylfurfuranedicarboxylic acid being formed, which therefore has the following constitution:

$$\mathrm{COO(C_2H_5).C:C(C_6H_5)}$$
$$\mathrm{COO(C_2H_5).C:C(C_6H_5)}\!>\!\mathrm{O}.$$

On saponification, this salt gives the acid $C_{18}H_{12}O_5$, thus:

$$C_{22}H_{20}O_5 + 2H_2O = C_{18}H_{12}O_5 + 2C_2H_5.OH.$$

The acid $C_{18}H_{12}O_5$ is therefore, without doubt, in reality diphenylfurfuranedicarboxylic acid.

The compound $C_{18}H_{10}O_4$, produced by the action of acetic anhydride on diphenylfurfuranedicarboxylic acid, is probably the anhydride of the acid, it being reconverted into the same by the action of alkalis. Its constitution would, therefore, be represented by the formula,

$$\mathrm{O}\!<\!\begin{array}{l}\mathrm{CO.C:C(C_6H_5)}\\ \mathrm{CO.C:C(C_6H_5)}\end{array}\!>\!\mathrm{O}.$$

A further examination of these compounds is, however, necessary before these points can be settled.

In the paper published in the *Berichte* (*loc. cit.*), the splitting off of the water was supposed to take place between the carboxyl-groups and the hydroxyl-groups in the compound $\begin{array}{l}\mathrm{COOH.C:C(OH)Ph}\\ \mathrm{COOH.C:C(OH)Ph}\end{array}$, the acid $C_{18}H_{12}O_5$ being a mono(γ)lactone and the compound $C_{18}H_{10}O_4$ a di(γ)lactone of dibenzoylsuccinic acid, and therefore having the formulae—

$$\mathrm{COOH.C}\!<\!\begin{array}{l}\mathrm{CH(CO.C_6H_5}\\ \mathrm{C(C_6H_5)-O}\end{array}\!>\!\mathrm{CO}$$

Mono(γ)lactone.

and

$$\mathrm{O}\!<\!\begin{array}{l}\mathrm{C(C_6H_5):C-CO}\\ \mathrm{CO-C:C(C_6H_5)}\end{array}\!>\!\mathrm{O}.$$

Di(γ)lactone.

From Knorr's experiments, however, it would seem that his explanation of the formation of these bodies is the most probable, and that they are furfurane-derivatives, and not lactones.

Ethylic Monobenzoylsuccinate.

The examination of this substance was undertaken in the hope of throwing further light on the constitution of the compounds mentioned in the preceding section. If the acid $C_{18}H_{18}O_8$ is the γ-lactone of dibenzoylsuccinic acid, it was thought probable that the corresponding γ-lactone of monobenzoylsuccinic acid might be obtained by the action of dilute sulphuric acid on ethylic monobenzoylsuccinate, thus:

$$CO(C_6H_5).CH<\begin{matrix}COOH\\CH_2.COOH\end{matrix} \qquad C(OH)(C_6H_5):C<\begin{matrix}COOH\\CH_2.COOH\end{matrix}$$

Benzoylsuccinic acid. Do. unstable form.

$$COOH.C<\begin{matrix}C(C_6H_5)\\CH_2.CO\end{matrix}>O.$$

γ-Lactone of benzoylsuccinic acid.

Ethylic benzoylsuccinate is easily obtained by treating the sodium compound of ethylic benzoylacetate with ethylic monochloracetate,

$$CO(C_6H_5).CHNa.COO(C_6H_5) + CH_2Cl.COO.C_2H_5 = CO(C_6H_5).CH(COO.C_2H_5).CH_2.COO.C_2H_5 + NaCl.$$

It was prepared as follows: 2.5 grams of sodium were dissolved in 30 grams of absolute alcohol, and then after well cooling, 20 grams of ethylic benzoylacetate and 12 grams of ethylic monochloracetate slowly added. The reaction takes place very slowly in the cold, but rapidly on a water-bath, the mixture after heating for two hours becoming perfectly neutral. In order to isolate the product, the alcohol was distilled off, and the residue then dissolved in water; by this means a heavy oil separated out, which was extracted with ether. After drying over calcium chloride and distilling off the ether, a thick brownish oil was obtained, which unfortunately could not be made to crystallise.

On trying to distil this in a vacuum, it was found that only a small quantity went over undecomposed, the principal part frothing up and charring, a quantity of gas being at the same time given off. It is, however, comparatively easy to distil small quantities of about 5 grams, if the distillation is rapidly conducted. The distillates from several such operations were united and fractioned

once or twice, when an oil was obtained boiling at 260–265° (160 mm.); this gave the following numbers on analysis, agreeing with the formula of ethylic benzoylsuccinate:

0.1557 gram substance gave 0.0905 gram OH_2 and 0.3695 CO_2.

	Found.	Theory.
C	64.72 per cent.	64.75 per cent.
H	6.46	6.47
O	28.82	28.78

As thus obtained, it is a thick, almost colorless oil, of an agreeable aromatic smell, somewhat resembling that of ethylic benzoate. It boils at 260–265° (at 160 mm.). The pure compound is very stable, and may be distilled at the ordinary pressure, apparently without much decomposition. It is insoluble in water, but mixes with alcohol, ether, and the usual solvents. As on examination it was found that the crude product consisted of almost pure ethylic benzoylsuccinate, and as the distillation entailed great loss of valuable material, the crude compound was used in the following reactions and decompositions, after the excess of ethylic benzoylacetate had been removed by shaking the ethereal solution several times with dilute potash solution.

On the addition of a drop of ferric chloride to the solution of ethylic benzoylsuccinate in alcohol a beautiful claret color is produced. If heated for some hours on an oil-bath at about 250°, ethylic benzoylsuccinate is decomposed, lower boiling aromatic oils being formed, which, however, could not be further examined, on account of the smallness of the quantity obtained. It dissolves in concentrated sulphuric acid, producing a yellow solution, which becomes intensely red when heated.

It is decomposed by heating with alcoholic potash, a violet solution being produced, which on acidifying deposits a solid acid melting at 118–120°, probably benzoic or benzoylpropionic acid.

Like ethylic dibenzoylsuccinate, ethylic monobenzoylsuccinate gives a sodium compound when treated with sodium ethoxide.

This compound is easily prepared in the following way; 0.3 gram of sodium is dissolved in a small quantity of absolute alcohol, and then pure dry ether added until the whole has nearly dissolved. A solution of 3.5 grams of ethylic benzoylsuccinate in ether is then poured in, and the whole allowed to remain for some time. The mixture becomes violet-colored, and a gelatinous precipitate slowly

separates, which is collected and washed, first with a mixture of ether and alcohol, and lastly with pure ether. Dried over sulphuric acid in a vacuum, it gave the following numbers:

0.2601 gram substance gave 0.0680 gram Na_2SO_4.

	Found.	Theory. $C_{18}H_{17}NaO_5$.
Na	8.47 per cent.	7.67 per cent.

It is a hard, almost colorless, apparently amorphous mass, which is moderately soluble in alcohol. If cupric acetate is added to this solution, the copper derivative is precipitated as a pale green amorphous mass, almost insoluble in water, but soluble in sodic hydroxide, producing a blue solution. Nitrate of silver and acetate of lead give white precipitates with the alcoholic solution of the sodium derivative. The sodium compound is very stable, much more so than the disodium derivative of ethylic dibenzoylsuccinate. The powdered substance is easily decomposed by treatment with acids, a yellowish oil being precipitated, probably regenerated ethylic monobenzoylsuccinate.

Decomposition Products of Ethylic Benzoylsuccinate.

Hydrolysis with Baryta-water.—Before examining the products of the hydrolysis with dilute sulphuric acid, it appeared to be interesting to study the action of alkalis, and for this purpose experiments were made with potash, but as this did not appear to give promising results, baryta-water was afterwards substituted for it, the method employed being the following:

Ethylic benzoylsuccinate was heated in a flask with an excess of a concentrated solution of barium hydroxide, by which means hydrolysis rapidly set in, the reaction being complete in about an hour. During the operation the oil disappeared, without the liquid becoming much discolored, and a heavy sandy precipitate of a brownish color slowly separated. This was collected, washed with water, and decomposed with hydrochloric acid, when traces of carbonic anhydride were given off. After extracting several times with ether, a dark-brown oil was obtained, which began to deposit crystals after some time. These were separated from the oily mother-liquor by extracting with chloroform, and thus obtained in a perfectly colorless state, melting at 180°, and having all the properties of succinic acid. In order to confirm this, the silver salt was prepared and analysed with the following result:

0.2024 gram substance gave 0.1306 gram silver.

	Found.	Theory, $C_4H_4O_4Ag_2$.
Ag	64.52 per cent.	65.07 per cent.

On acidifying with hydrochloric acid the filtrate from the precipitated baric succinate, it gave a quantity of a beautifully crystalline acid, which was collected, well washed, and recrystallised once or twice from water. It was thus obtained in silky needles melting at 118–120°, and was therefore either benzoic or benzoylpropionic acid. A silver salt was made and analysed with the following result:

0.1976 gram substance gave 0.0936 gram silver.

	Found.	Theory, C_6H_5COOAg.	Theory, $C_6H_5.CO.CH_2.CH_2.COOAg$.
Ag	47.37 per cent.	47.16 per cent.	37.82 per cent.

The acid was evidently benzoic acid.

Ethylic benzoylsuccinate is therefore decomposed by boiling with concentrated baryta-water into benzoic and succinic acids, thus:

$$C_6H_5.CO.CH(COO.C_2H_5).CH_2.COO.C_2H_5 + 3H_2O = C_6H_5.COOH + C_2H_4(COOH)_2 + 2C_2H_5.OH.$$

In this respect it differs somewhat from ethylic acetylsuccinate, which on hydrolysis with dilute baryta-water, is split up into acetylpropionic acid and carbonic anhydride, only a small quantity of acetic acid and succinic acid being formed.[1]

Ethylic benzoylsuccinate, if treated with dilute baryta-water, might also be split up in this way into benzoylpropionic acid and carbonic anhydride.

Hydrolysis with Dilute Sulphuric Acid.—Ethylic benzoylsuccinate was heated with a large excess of dilute sulphuric acid (1 : 2) in a flask connected with a reflux condenser, at the end of which a test-tube containing baryta-water was attached. The oil became more and more darkly colored, and large quantities of carbonic anhydride were given off, until at the end of about fifteen hours most of the ethereal salt had dissolved, a small quantity of a tarry substance being left. On cooling, the liquid became filled with glittering crystals, which were collected, well washed with water, roughly separated from oily mother-liquor by spreading

[1] Conrad, Annalen **118**, 218.

out on a porous plate, and then recrystallised once or twice from water, animal charcoal being used to decolorise the liquid. In this way, the body was obtained in glittering plates melting at 117°, and closely resembling benzoic acid. The analysis, however, showed the body to be benzoylpropionic acid.

0.2230 gram substance gave 0.1132 gram OH_2 and 0.5487 gram CO_2.

	Found.	Theory, $C_{10}H_{10}O_3$.
C	67.12 per cent.	67.41 per cent.
H	5.64	5.62
O	27.24	26.97

Ethylic benzoylsuccinate splits up, therefore, on boiling with dilute sulphuric acid into benzoylpropionic acid and carbonic anhydride according to the equation—

$$CO(C_6H_5).CH(COO.C_2H_5).CH_2.COO.C_2H_5 + 2H_2O = CO.C_2H_5.CH_2.CH_2.COOH + CO_2 + 2C_2H_5.OH.$$

Benzoylpropionic acid has already been obtained (1) by the action of aluminic chloride on a mixture of succinic anhydride and benzene,[1] and by the reduction of benzoylacrylic acid.[2] The acid obtained from ethylic benzoylsuccinate agrees with that produced by the above two reactions in every respect.

By modifying the conditions in the hydrolysis of *ethylic benzoylsuccinate* with dilute sulphuric acid, the same results were always obtained, no lactone ever being formed. The reason for this is that the C_2H_5 group of the $COO.C_2H_5$, which is joined to the $C_6H_5.CO.CH$, in benzoylsuccinic ether, is always split off first, forming the unstable acid $C_6H_5.CO.CH(COOH).CH_2.COO.C_2H_5$, which then naturally loses carbonic anhydride, and is converted into ethylic benzoylpropionate, this being then further hydrolysed by the action of the sulphuric acid. Analogous results were obtained by Conrad[3] by the action of dilute sulphuric acid on ethylic acetylsuccinate, acetylpropionic acid, ethylic acetylpropionate and carbonic anhydride being the products of the reaction.

[1] Burcker, Bull. Soc. Chim. **35**, 17. [2] Pechmann, Ber. **14**, 889. [3] Ber. **11**, 2177.

[*To be continued.*]

ON THE DETERMINATION OF ARSENIC.

By LeRoy W. McCay.

Arsenic and its compounds have until lately proved very unsatisfactory things for the chemist to determine. There are indeed few common elements the quantitative estimation of which has, up to within the last few years, presented such numerous, persistent and extraordinary difficulties as the one forming the subject of this paper. As a matter of fact there is, at the present day, no gravimetric method for estimating arsenic which is not without fault. The one most commonly used, that of Levol, is, open to at least two serious objections. In the first place, the ammonium magnesium arseniate is perceptibly soluble in ammonia water, and in the second place, the danger of occasioning a loss of arsenic by the reducing action of the ammonia upon igniting the salt is a fact too well known to need mention. Chemists, it will be remembered, have endeavored to avoid the error arising in the first instance by the addition of alcohol to the solution to be precipitated, but even in ammoniacal alcohol the double arseniate is sensibly soluble; consequently, although considerably reduced, the error cannot be said to be entirely eliminated. Attempts have also been made, and that too with a considerable amount of success, to avoid the error arising in the second instance by removing the salt particles adhering to the filter paper with dilute nitric acid, moistening the precipitate with the same reagent, and igniting—at first gently, then strongly. Much skill and care, however, is requisite in the process of igniting; it being no uncommon occurrence, when the heat is too suddenly applied, to drive off a portion of the ammonia at such a rate as to occasion considerable reduction, even in such a strong oxidising atmosphere as nitrous oxide.[1]

Not long since Bunsen[2] published an article upon the separation of arsenic and antimony and upon the determination of each as sulphide. The separation of the two elements is quick, easy and

[1] Brauner, who proposes the igniting of the precipitate in an atmosphere of nitrous oxide, directs that the salt be brought into a small thin porcelain crucible, that this crucible be placed in a larger one of platinum, and that the heat be then applied, very gently at first, then gradually stronger, until the full capacity of the burner is reached.

[2] Zeitschr. f. analy. Chem. **16**, 57. See also Reichel, Zeitschr. f. analy. Chem. **20**, 89.

accurate. As regards the estimation of the arsenic, however, it is, as Fresenius has already intimated, undoubtedly necessary, in order to ensure correct results, to follow Bunsen's details to the letter; for although the sulphide obtained by precipitating the arsenic from a solution thoroughly treated with chlorine has, after having undergone a detailed course of washing, exactly the composition of arsenic pentasulphide, and is in fact regarded by Bunsen as being such, it must not be forgotten that no less an authority than Rose[1] declares the precipitate occasioned by sulphuretted hydrogen in solutions of arsenic acid to be not pure arsenic pentasulphide, As_2S_5, but a mixture of the trisulphide, As_2S_3, and sulphur. If Rose's statement is true, then the chances are that a slight departure from the directions as given by Bunsen might occasion incorrect results in the determination of the element. Besides the objection to be found in the uncertainty as to the actual character of the sulphide obtained by neglecting to follow Bunsen's details absolutely, another and serious one can be urged against the necessity of being compelled to weigh the precipitate on a tared filter paper after having thoroughly dried at 110° C. I willingly grant that the Bunsen method furnishes perfectly correct results, and that it is a wonderful improvement upon the old method of Levol; still it is a long, tedious and unpleasant operation. The arsenic is precipitated very slowly from the solution of arsenic acid, and unless the precipitate is filtered off at just the right point some arsenic is sure to remain in solution. The precipitation, in fact, requires much attention, patience and practice, and in consequence thereof it is with much pleasure and satisfaction that we welcome the beautiful proposal of Carl Holthof.[2]

Mohr's method for estimating arsenic is one of the most simple and exact in the field of analytical chemistry. It presupposes, however, the existence of the arsenic in the state of arsenious acid, a condition which is rarely fulfilled inasmuch as in the regular course of analysis arsenic is almost invariably obtained as arsenic trisulphide or arsenic acid. The method, it will be remembered, depends upon the fact that in a weakly alkaline solution arsenic in

[1] Rose, Pog. Ann. **107**, 186. Wackenroder arrived at the same results prior to Rose. See Ludwig's investigations, Ar. d. Pharm. 2 Reihe, **97**, 32. Also A. Fuchs, Zeitschr. f. analy. Chem. **81**, 189.

[2] Holthof, Zeitschr. f. analy. Chem. **23**, 378.

the state of arsenious acid is oxidised by iodine to arsenic acid, in accordance with the equation:

$$H_3AsO_3 + 2I + H_2O = H_3AsO_4 + 2HI.$$

The difficulty of obtaining the arsenic in the minimum state of oxidation has caused the method of Mohr to fall into neglect and consequently escape that attention which is due it.

Many years ago Holthof obtained very satisfactory results by carefully oxidising small quantities of sulphide of arsenic with nitric acid in a porcelain dish, evaporating to dryness with a few drops of sulphuric acid, and boiling down in a large beaker to one-third the original volume, after having first added one-third of a litre of sulphurous acid solution, then refilling to the mark with sulphurous acid solution, and again evaporating to one-third the original volume, neutralising, after cooling, with sodium carbonate, adding a constant quantity of mono-sodium carbonate, a little starch solution, and titrating with a standard solution of iodine. Holthof evidently did not at that time publish anything relating to this method of determining arsenic, for in speaking of it in the first part of his recent paper he makes no reference to any work or periodical. A little over a year ago, at the instigation and in the laboratory of Fresenius in Wiesbaden, he undertook a thorough study of the process, it being his chief object to discover whether the mode of procedure was applicable in the case of large quantities of arsenic, and also practicable in determining the arsenic in the strong hydrochloric acid solution which is obtained when working according to the Bunsen separation method. It will be at once evident that the success of the method depends upon the complete reduction of the arsenic from the arsenic to the arsenious state of oxidation. Holthof starts out with the assumption[1] that when a sufficient quantity of sulphurous acid is used, and the solution is heated for a sufficient length of time, the reduction is complete, and in the end he proves that this is the case.

In brief Holthof's method is as follows: 1. The solution containing about 0.10–0.20 gram arsenious oxide, As_2O_3, as arsenic oxide, As_2O_5, is brought to 50 cc. and diluted in a flask with 100–150 cc. sulphurous acid and 150–200 cc. water. The flask with its contents is then heated for four hours, and next boiled down over a free flame to one-half the original volume. A little clear starch

[1] See the communication of Wöhler, Ann. d. Chem. und Pharm. **30**, 224.

solution is now run in, 40 cc. of a solution of hydro-sodium carbonate saturated in the cold added, the whole diluted to about one-third of a litre and titrated to a light sky-blue, with a standard solution of iodine containing approximately 10.0 grams iodine to the litre. The test analyses, although not numerous, are very satisfactory.

2. Holthof did not experiment upon sulphide of arsenic, at all events not in the case before us, but his thorough study of the oxidising action of chlorine upon the arsenious acid, and his examination of the question relating to the volatility of arsenic trichloride when a solution of arsenic acid is evaporated to dryness with excess of hydrochloric acid, justify us in presuming that, according to him, the following would be the method of procedure in the case of sulphide of arsenic.[1] The sulphide of arsenic is brought into a little porcelain dish provided with a watch-glass cover, and treated either with fuming nitric acid or potassium chlorate and hydrochloric acid until solution is complete. The liquid is then evaporated, a few drops of sulphuric acid added, diluted, reduced as already described, boiled down to one-half the original volume, cooled, evaporated to about 300 cc., and titrated to a light blue. The test analyses resulting from evaporating arsenic pentoxide, As_2O_5, solutions in the presence of excess of chlorine and hydrochloric acid are good, and prove conclusively that when arsenic acid, chlorine and hydrochloric acid are evaporated upon the water-bath no arsenic is volatilised as trichloride. The two sets of experiments then prove:

1st. That the reduction with sulphurous acid is complete; 2d. that upon evaporating arsenic pentoxide, As_2O_5, in the presence of hydrochloric acid, no arsenic escapes as trichloride.

Holthof concludes from the above that not only is the method suitable for technical needs, but also that its exactness renders it worthy of being used for scientific purposes.

For some time past I have been engaged in making a thorough examination of the method of Holthof, and I have reached the conclusion that it is the most perfect one at present known. Further, by taking advantage of a device of my own, the time requisite for making a determination is reduced to a minimum. At the outset I went over Holthof's work for the purpose of

[1] See his method of procedure as practised in former years.

determining whether the reduction, when made in strict accordance with his directions, is so complete as to render it impossible to detect, by qualitative measure, any arsenic acid in the liquid after boiling down to one-half the original volume and then carefully evaporating to about 50 cc.

In order to obtain a solution suitable for qualitative as well as quantitative experiments, I dissolved 28.90 grams H_2KAsO_4 in about 250 cc. water and diluted to two litres. Theoretically every 10 cc. of this solution should contain 0.0602 gram As = 0.0794 gram As_2O_3 = 0.0923 gram As_2O_5. However, being ignorant as to the exact degree of purity of the salt, the solution was carefully analysed: 1st. by the method of Levol; 2d. by the method of Reich.

1st. 10 cc. were put into a small beaker, rendered strongly acid with hydrochloric acid, then strongly alkaline with ammonia, cooled, and finally precipitated with magnesia mixture, care being taken to add this reagent slowly, drop by drop, and with constant stirring. After standing twelve hours the ammonium magnesium arseniate was filtered off, washed with ammoniacal water, dried, moistened with nitric acid and ignited—all details relating to the extraction of the particles of the salt from the filter paper with dilute nitric acid being strictly observed. The 10 cc. gave 0.1215 gram $Mg_2As_2O_7$ = 0.0591 gram As = 0.0780 gram As_2O_3 = 0.0906 gram As_2O_5. These figures, it will be observed, are somewhat lower than those required by theory.

2d. *Three Estimations.*—*a.* One volumetrically; *b.* two gravimetrically.

a. 10 cc. were put into a small beaker, about 50 cc. water added, and enough ammonia to produce a decided alkaline reaction dropped in. The solution was then heated to boiling, and a quantity of silver nitrate sufficient to ensure complete precipitation of the arsenic run in. The liquid was now stirred briskly until the precipitate exhibited a tendency to settle, leaving the supernatant fluid clear. The beaker with its contents was next removed from the flame, and ammonia water added to faint but distinct alkaline reaction. This alkaline reaction was removed by the aid of a drop of acetic acid, the liquid again thoroughly stirred, the whole allowed to stand for a few minutes, and, after entire subsidence, the silver arseniate filtered off, washed with pure cold water, dissolved off the filter paper with a little dilute nitric acid,

and the combined silver determined according to Volhard.[1] I found 0.2572 gram Ag = 0.0595 gram As = 0.0785 gram As_2O_3 = 0.0912 gram As_2O_5. The method of neutralising the solution is my own.

b. For the two estimations made gravimetrically and according to my own modification[2] of the Reich process, I used in each case 10 cc. The precipitation of the arsenic was made exactly as above described, but instead of dissolving the silver arseniate in nitric acid and titrating the silver, the precipitate was removed from the filter paper by means of a few drops of ammonia and a little water, the solution caught in a small weighed platinum dish, evaporated to dryness, the residue heated for a short time at 100° C. and then weighed. From the formula Ag_3AsO_4 the arsenic was calculated. I found (1) 0.3661 gram Ag_3AsO_4 = 0.0592 gram As = 0.0781 gram As_2O_3 = 0.0907 gram As_2O_5; (2) 0.3659 gram Ag_3AsO_4 = 0.0592 gram As = 0.0781 gram As_2O_3 = 0.0907 gram As_2O_5. Since the molecular weight of Ag_3AsO_4 = 463, and the atomic weight of As = 75, the relation between the two is about 6:1, or a difference of six milligrams in the weight of the silver salt will occasion a difference of but one milligram in the weight of the arsenic. The wonderful degree of accuracy of the method is at once evident. The Levol method gave 0.0591 gram metallic arsenic; the Reich method 0.0593 gram of the element in 10 cc. The difference, 0.0002 gram, is due probably to the solubility of the ammonium magnesium arseniate in ammoniacal water. The figure 0.0593 is undoubtedly the correct one, and we shall in our future work regard it as such.

The following are the *qualitative* tests made according to Holthof's directions, my object here being, as already intimated, to satisfy myself as to the exact degree of completeness of the reduction of the arsenic from the arsenic to the arsenious state of oxidation. In I, each of the 10 cc. of H_2KAsO_4 solution taken were mixed in a flask with 50 cc. sulphurous acid and 100 cc. water, after which the flask and contents were heated for two hours upon the boiling water-bath, then for two hours to incipient boiling upon a little sand-bath, whereupon the liquid was boiled down over a free flame to one-half the original volume; a large platinum

[1] Pearce's modification of the Reich method: For particulars see Engineering and Mining Journal **35**, 256. See also Chemical News **48**, 85.

[2] For another modification see Chemical News **48**, 7 and 168.

spiral with pieces of pumice about the size of hazel-nuts threaded and twisted on each end being introduced into the flask, partially to prevent bumping, partially to facilitate the disengagement of the sulphur-dioxide gas. In II, double the quantities of sulphurous acid and water used in I were added, and in III, first the quantities used in I, second those used in II. In each case the liquid remaining after boiling down was emptied into a porcelain dish, evaporated to about 50–60 cc. and tested for arsenic acid (1) with silver nitrate, (2) with magnesia mixture, and (3) with magnesia mixture after removing the arsenic as the trisulphide with sulphuretted hydrogen in the cold and displacing the latter with a rapid stream of carbon dioxide. The tests were made in strict accordance with the directions of Fresenius.[1] In no case was I able to obtain in the 50–60 cc. a decided reaction for arsenic acid. For sake of convenience I arrange the experiments in outline as follows:

I.

a. 10 cc. solution, 50 cc. SO_2 and 100 cc. H_2O.
b. " " " "

a. Reaction for As_2O_5 with $AgNO_3$, none. *b.* Reaction for As_2O_5 with magnesia mixture, none.

II.

a. 20 cc. solution, 100 cc. SO_2 and 200 cc. H_2O.
b. " " " "

a. Reaction for As_2O_5 with $AgNO_3$, none. *b.* Reaction for As_2O_5 with magnesia mixture, none.

III.

a. 10 cc. solution, 50 cc. SO_2 and 100 cc. H_2O.
b. 20 cc. solution, 100 cc. SO_2 and 200 cc. H_2O.

a. Reaction for As_2O_5 with magnesia mixture, after separation of As_2O_3, none. *b.* Reaction for As_2O_5 with magnesia mixture, after separation of As_2O_3, none.

These experiments go to prove that the reduction of the arsenic from the arsenic to arsenious state is to all intents and purposes complete, and in consequence thereof they confirm conclusively

[1] Fresenius, Anleitung zur qualit. chem. Analyse, 14 Aufl. **199**, 9.

what Holthof has to say respecting the correctness of his mode of procedure. For quantitative work much experience has led me to believe that the following solutions are probably the most convenient:

(*a*) $\frac{1}{40}$ *Normal iodine solution.*[1]—Dissolve 6.35 grams of pure dry iodine with the help of about 10.0 grams of potassium iodide in a little water and dilute to a litre.

(*b*) $\frac{1}{40}$ *Normal arsenious oxide solution.*[1]—Dissolve 2.475 grams chemically pure arsenious oxide in a little warm potassium hydrate solution, neutralise with hydrochloric acid and dilute to a litre.

Use for controlling the iodine solution:

(*c*) *Starch solution.*[2]—Rub up thoroughly in a small porcelain mortar, with 10 cc. of a solution of pure potassium hydrate of ordinary strength, two grams of starch and bring into 200 cc. boiling water. Stir until solution is complete, cool bottle and preserve well corked. It will keep indefinitely.

(*d*) *Hydro-sodium carbonate.*—Dissolve 150–200 grams of the pure salt in two litres of water.

(*e*) *Sulphurous acid.*—Use water *saturated*[3] with the gas.

Theoretically, 1 cc. of the above $\frac{1}{40}$ normal iodine should exactly balance 1 cc. of the $\frac{1}{40}$ normal arsenious oxide, and 1 cc. = 0.001875 gram As = 0.002475 gram As_2O_3 = 0.002875 gram As_2O_5; practically, however, 20 cc. of the arsenious oxide solution required, in three separate trials, (1) 19.9, (2) 19.9, and (3) 19.9 cc. of the iodine solution for complete oxidation. Hence 1 cc. = 0.001884 gram As = 0.002487 gram As_2O_3 = 0.002889 gram As_2O_5.

A. 1.—50 cc. of the solution H_3KAsO_4, 100 cc. SO_2 and 150 cc. water were brought into a flask and heated for two hours upon a boiling water-bath, then for two hours upon a little sand-bath, and finally boiled down to one-half the original volume, a large platinum spiral being introduced into the flask to prevent bumping and facilitate the disengagement of the sulphur-dioxide gas. In all my experiments this boiling down to one-half the original volume (care being of course taken to introduce into the flask the platinum spiral) proved amply sufficient. I have not yet been able to detect any sulphur dioxide in a solution so treated.

[1] Modern system. See Clemens Winkler's Maassanalyse, Freiberg, 1883.

[2] Alex. Müller, Landw. Versuchs-Stationen **27**, 340. See also Zeitschr. f. analy. Chem. **22**, 76.

[3] This solution should be as strong as possible.

The solution was allowed to cool, diluted to 300 cc., and for each of the first lot of estimations below given 30 cc., for each of the second lot 60 cc. taken. In tritrating care was taken always to work under like conditions—the same quantities of hydro-sodium carbonate, starch and water being invariably used. The most convenient volume of liquid for titration proved to be approximately 300 cc. Accordingly, 30 cc. reduced solution, 20 cc. hydro-sodium carbonate and 1 cc. starch solution being diluted in a larger beaker to 300 cc., the $\frac{1}{40}$ normal iodine solution was run in until a sky-blue color resulted. The point of transition is remarkably easy to strike, and the reaction is so sharp and exact that one is never in doubt as to a single drop. The fact too that the blue appears shortly before the oxidation is complete and a little extra stirring is necessary to cause it to disappear, furnishes us with an indication of the approach of the end of the operation, and thereby renders it almost impossible for one to overstep the point.

Four estimations:

No.	Red. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	30 cc.	15.7 cc.	0.0295 gram.	0.0390 gram.	0.0453 gram.
2	30	15.7	0.0295	0.0390	0.0453
3	30	15.7	0.0295	0.0390	0.0453
4	30	15.75	0.0296	0.0391	0.0454

Actually present:

$$As = 0.0296 = 0.0390,\ As_2O_3 = 0.0453\ As_2O_5.$$

Three estimations:

No.	Red. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	60 cc.	31.5 cc.	0.0593 gram.	0.0783 gram.	0.0910 gram.
2	60	31.5	0.0593	0.0783	0.0910
3	60	31.6	0.0595	0.0785	0.0915

Actually present:

$As = 0.0593$ gram $= 0.0782$ gram, $As_2O_3 = 0.0907$ gram As_2O_5.

2.—100 cc. H_2KAsO_4, 150 cc. SO_2 solution and 200 cc. water were brought into a flask and reduced as above described. After boiling the liquid down to one-half the original volume, cooling and diluting to 1000 cc., the following results were obtained. For each determination 100 cc. solution were taken.

No.	Red. Solution	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	100 cc.	31.7 cc.	0.0597 gram.	0.0788 gram.	0.0916 gram.
2	100	31.8	0.0599	0.0791	0.0918
3	100	31.7	0.0597	0.0788	0.0916
4	100	31.8	0.0599	0.0991	0.0918

50 cc. of same solution required 15.9 cc. $\frac{1}{40}$ normal iodine = 0.02995 As = 0.0395 As_2O_3 = 0.0459 As_2O_5.

The average number of cc. of $\frac{1}{40}$ normal iodine used in this lot of tests is 31.75, the average number used in the lot immediately preceding is 31.53; the difference between the two is 0.22 cc. This 0.22 is a distinct plus, and requires explanation in spite of the fact that owing to the extremely dilute iodine solution it is too small to occasion any decidedly appreciable error in the results. The excess is, I am inclined to believe, probably due to the action on the iodine of organic matter in the distilled water, the destructive capacity of this matter as regards iodine increasing, as a matter of course, with the increase in the quantity of water used, as well as with the length of time requisite for reducing and boiling down to the required volume. It will be observed that in the second experiment more water was used than in the first, and in consequence thereof that the time necessary for reducing and boiling down is greater in the latter than in the former case.

B. 1.—To test the method further, I brought 2.475 grams As_2O_3 into a litre-flask with a long, narrow neck, added 100 cc. pure nitric acid, and, having clamped the flask in an inclined position in the water-bath, heated the contents to boiling. As soon as all reaction had ceased, the flask and contents were removed from the bath, and heated gently over a free flame until all hyponitric oxide fumes had disappeared and the solution was clear and colorless. 20 cc. dilute sulphuric acid were then added, the solution was transferred to a porcelain dish, evaporated down until every trace of nitric acid was expelled, cooled, neutralised, and diluted to a litre. 50 cc. of this solution were mixed with 150 cc. SO_2 solution, 200 cc. water added, and the whole was treated as already described —for two hours on the water-bath, two hours on the sand-bath, and finally boiled down over a free flame to a little less than one-half the original volume. The liquid after cooling was diluted to exactly 200 cc., and for each of the following tests 50 cc. taken.

No.	Red. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	50 cc.	12.5 cc.	0.0235 gram.	0.0311 gram.	0.0361 gram.
2	50	12.5	0.0235	0.0311	0.0361
3	50	12.5	0.0235	0.0311	0.0361
4	50	12.5	0.0237	0.0313	0.0363

Since 1000 cc. standard solution = 2.475 grams As_2O_3, 50 cc. =

0.12375 gram As_2O_3; and since the 50 cc. were after reduction and boiling down diluted to 200 cc., 50 cc. or $\frac{1}{4}$ of 200 cc. = 0.0309 gram As_2O_3, a figure which agrees very well with that found by analysis.

2. 100 cc. standard solution, 200 cc. SO_2 solution and 200 cc. water were reduced, boiled down, cooled and diluted to 500 cc. Four tests were made, each with 100 cc.

No.	Red. Solution.	$\frac{1}{10}$ Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	100 cc.	20.1 cc.	0.0378 gram.	0.0499 gram.	0.058 gram.
2	100	20.1	0.0378	0.0499	0.058
3	100	20.05	0.0377	0.0498	0.058
4	100	20.1	0.0378	0.0499	0.058

Theory demands:

$$0.0375\ As = 0.0495\ As_2O_3 = 0.0575\ As_2O_5.$$

20 cc. of the standard solution should require, after reduction, 19.9 cc. $\frac{1}{10}$ normal iodine, whereas, as will be seen, 20.1 cc. were used. The cause of the error, 0.22 cc., has already been suggested. The error is so small that it in no case materially affects the accuracy of the results.

Having had occasion during my examination of the Holthof method to subject several organic compounds at high temperatures and under pressure to the oxidising influence of certain reagents, the thought suggested itself that, perhaps, by acting on arsenic acid with sulphurous acid under pressure, the reduction of the former to the lower stage of oxidation might be easily accomplished, and that too in a comparatively short period of time. The results of some qualitative experiments in this direction will be found in the *Chemical News*, Vol. 51, No. 1320, March 13th, 1885. The results obtained were very satisfactory, and seemed to prove without a doubt that when arsenic acid, sulphurous acid and water are heated for one hour in hermetically closed flasks and at a temperature equal to that of boiling water, the arsenic acid is completely reduced to arsenious acid. In my article in the *Chemical News* I have given the results of seven experiments, the quantity of arsenic as arsenic acid in each test ranging from 0.06 to 0.90 gram. In every case excepting one the reduction was complete. In the last experiment (0.9 gram arsenic acid present) 20 cc. of the reduced solution gave with magnesia mixture, after

boiling off the sulphur dioxide, a slight reaction for arsenic acid —one so slight, however, that upon filtering off the precipitate and dissolving it in a drop of nitric acid, no reddish-brown color or precipitate was obtained with silver nitrate and ammonia. In all the seven experiments my tests were made upon *portions* of the reduced solution, consequently it seemed well before trying the process quantitatively, again to make a series of experiments, using the entire quantity of the reduced liquid for a test exactly as was done in my examination of the Holthof method of reduction.

I proceeded as follows.

The solution of H_2KAsO_4 was brought into a little bottle provided with a well-fitting ground-glass stopper, and capable of withstanding a pressure corresponding to the heat of a boiling water-bath, a strong solution of sulphurous acid run in, the bottle tightly stoppered and the stopper firmly tied down with a piece of cord. The bottle was next placed in a water-bath, the contents of which had been brought to active boiling, and here permitted to remain for exactly one hour. After cooling, the reduced liquid was emptied into a flask, diluted to about 150 cc. and boiled down to one-half the volume, care being taken to introduce into the flask a large platinum spiral. It was then transferred to a porcelain dish, evaporated to 50 cc., filtered, and tested for arsenic acid (1) with silver nitrate, and (2) with magnesia mixture.[1] Six tests were made, but in no case could I, after boiling down, obtain in the 50 cc. a definite reaction for arsenic acid.

I.

10 cc. H_2KAsO_4 solution;
20 cc. SO_2 solution.

10 cc. = 0.0593 gram As = 0.0782 gram As_2O_3 = 0.090 gram As_2O_5.

Reaction for As_2O_3 with silver nitrate, none.

II.

10 cc. H_2KAsO_4 solution;
20 cc. SO_2 solution.

10 cc. = 0.0593 gram As = 0.0772 gram As_2O_3 = 0.090 gram As_2O_5.

Reaction for As_2O_3 with magnesia mixture, none.

[1] The solutions stood 12—24 hours.

III.

20 cc. H_2KAsO_4 solution;
30 cc. SO_2 solution.

20 cc. = 0.1186 gram As = 0.1564 gram As_2O_3 = 0.180 gram As_2O_5.

Reaction for As_2O_5 with silver nitrate, none.

IV.

20 cc. H_2KAsO_4 solution;
30 cc. SO_2 solution.

20 cc. = 0.1186 gram As = 0.1564 gram As_2O_3 = 0.180 gram As_2O_5.

Reaction for As_2O_5 with magnesia mixture, none.

V.

30 cc. H_2KAsO_4 solution;
40 cc. SO_2 solution.

30 cc. = 0.1779 gram As = 0.2346 gram As_2O_3 = 0.270 gram As_2O_5.

Reaction for As_2O_5 with silver nitrate, none.

VI.

30 cc. H_2KAsO_4 solution;
40 cc. SO_2 solution.

30 cc. = 0.1779 gram As = 0.2346 gram As_2O_3 = 0.270 gram As_2O_5.

Reaction for As_2O_5 with magnesia mixture, none.

Having worked so satisfactorily qualitatively, I determined to see whether this method of reduction could not be made to take the place of that suggested by Holthof; it being plain that, should its practicability prove incontestable, the Mohr-Holthof process would be wonderfully improved, especially in respect to the time necessary for making a reduction. When working according to Holthof, considerable quantities of sulphurous acid and *four* hours are requisite for complete reduction; whereas, by subjecting the arsenic acid under pressure to the reducing influence of the sulphurous acid, the reduction is accomplished in *one* hour. It is just here that I propose to modify the method.

Since the reduction of arsenic to arsenious acid with sulphurous acid is, when all the details above indicated are strictly observed,

not only complete, but also capable of being carried out in a remarkably short period of time, it seemed feasible to make a few estimations of the element as the sulphide; this method of determining the arsenic being especially applicable in the case of a solution containing pure arsenious acid, and free from all substances possessing the property of acting in a reducing manner upon sulphuretted hydrogen.

The determinations were made by bringing the solution of H_2KAsO_4 into a little bottle of convenient size, adding somewhat over an equal volume of *strong* sulphurous acid and reducing, then boiling down one-half after transferring to a flask, and precipitating the arsenic in a beaker with freshly prepared sulphuretted hydrogen water. The solution when ready for precipitation should be moderately hot, strongly acid, and its volume should equal about 100 cc. The freshly prepared and perfectly clear sulphuretted hydrogen water is to be added in slight excess, and the solution, after the addition of the same, heated on the sand-bath to about 80–85°, and kept at this temperature with occasional stirring until the precipitate of the sulphide settles completely, leaving the supernatant fluid clear, and emitting but a faint odor of sulphuretted hydrogen. The filtrates, although invariably examined, gave no evidence of the presence of arsenic.

Friedrich Mohr, in his *Lehrbuch der Titrirmethode*, IV Auflage, S. 357, uses the following language: "When the arsenic as arsenic trisulphide is once gotten upon the filter paper, nothing is simpler than to dissolve the same off the paper in ammonic hydrate and evaporate the resulting solution to dryness in a watch-glass or porcelain dish. I have satisfied myself that *dry* arsenic trisulphide when weighed in a platinum dish, dissolved in ammonic hydrate and again evaporated to dryness, gives exactly the same weight. From 0.243 gram As_2S_3 I obtained 0.243 gram, from 0.643 gram I got back 0.642 gram. It is only the filter paper which hinders the weighing and drying, and this is here done away with." Neither Rose, Fresenius nor Classen recommends this method of treating the precipitate of the sulphide, and I therefore thought it well to put it to the test. I made six determinations, the ammoniacal solution being caught, evaporated and weighed in a thin, light platinum dish. The sulphide was not dried, but dissolved off the paper as soon as the washing was finished. Mohr's experiments were made on the *dry* sulphide, although from his

directions one would conclude that he advocated too the direct application of the ammonia to the still moist precipitate. Whether or not correct results would be obtained by first drying and then dissolving the precipitate I am unable to say. The following are the results of my experiments:

No.	St. Sol.	As_2S_3.	As.	As_2O_3.	As_2O_5.
1	10 cc.	0.0965 gram.	0.0588 gram.	0.0776 gram.	0.0901 gram.
2	10	0.0955	0.0582	0.0768	0.0892
3	10	0.0963	0.0586	0.0774	0.0898
4	10	0 0945	0.0576	0.0759	0.0883
5	10	0.0985	0.0600	0.0792	0.0920
6	10	0.1003	0.0611	0.0806	0.0936

10 cc. = 0.0593 gram As = 0.0782 gram As_2O_3 = 0.0907 gram As_2O_5.

The above results are not only incorrect, but they exhibit no constancy among themselves, in spite of the fact that in all cases extreme care was taken to work under like conditions. During the evaporation of the ammoniacal solution, one of the first things which attracted any attention was an evolution of sulphuretted hydrogen which continued until the last traces of moisture had disappeared and the residue exhibited a perfectly dry appearance. The presence of the sulphuretted hydrogen could be distinctly indicated by the change of color to brown, and in some cases almost to black, of a piece of filter paper moistened with a little acetate of lead solution and held over the platinum dish containing the solution of arsenic. The figures above given show conclusively that Mohr's proposal is inapplicable, at all events in the case of freshly precipitated and still moist trisulphide of arsenic. Numbers 1, 2, 3 and 4 are too low; number 5 is very nearly correct; while number 6 is too high. In Roscoe and Schorlemmer's *Treatise on Chemistry*, Vol. I, page 538, I find that no less a man than Wöhler directs that the sulphide of arsenic obtained in *forensic work* be dissolved off the filter paper in ammonia, the resulting solution evaporated in a dish, and the element weighed as the trisulphide, As_2S_3. *No mention whatever is made of its being necessary first to dry the precipitate.* It is a very remarkable fact that the evolution of sulphuretted hydrogen during the evaporation of the ammoniacal solution should have escaped the notice of Mohr and Wöhler, and it is likewise a remarkable fact that no one has yet seen fit to call

attention to the inaccuracy involved in weighing the arsenic as the compound obtained by evaporating an ammoniacal solution of the trisulphide.

However, by following the usual method, collecting, drying and weighing on a tared paper, very satisfactory results were obtained, as the figures below given will at once show. I find it well, after a thorough washing, to remove the adhering water by means of about 10 cc. of absolute alcohol so as to hasten the subsequent drying of the precipitate. The sulphide was weighed in a very light drying-box provided with a well-fitting ground-glass stopper.

No.	St. Sol.	As_2S_3	As.	As_2O_3.	As_2O_5.
1	20 cc.	0.1935 gram.	0.1180 gram.	0.1553 gram.	0.1810 gram.
2	20	0.1930	0.1176	0.1550	0.1802
3	20	0.1940	0.1182	0.1560	0.1812

20 cc. = 0.1186 gram As = 0.1564 gram As_2O_3 = 0.1814 gram As_2O_5. With 50 cc. H_2KAsO_4 solution I obtained 0.4869 gram As_2S_3 = 0.2963 As = 0.391 As_2O_3 = 0.4527 As_2O_5.

I shall now return to my modification of the Holthof method of reduction.

To avoid then the large quantities of sulphurous acid necessary when working according to Holthof, and, moreover, render it possible to effect the reduction of the arsenic from the maximum to the minimum stage of oxidation in one-fourth the time hitherto considered requisite, I suggest that Holthof's method be so modified that the reduction be accomplished in hermetically sealed bottles and at a temperature equal to that of boiling water. Qualitative as well as gravimetric quantitative experiments have already proved the reduction to be fully as complete as the one proposed by Holthof, and since its advantages over the Holthof method have been clearly pointed out, it only remains for me to offer a number of test analyses, obtained under various conditions, by titrating different quantities of known solutions of reduced arsenic acid with $\frac{1}{40}$ normal iodine.

A. 1.—In making the following lot of tests the solution of H_2KAsO_4 was brought into a small bottle provided with a well-fitting ground-glass stopper, and capable of holding when filled filled 50 cc.; 20 cc. of sulphurous acid were added, the bottle was tightly stoppered and the stopper firmly tied down with a piece of stout cord. The bottle with its contents was then placed in the

briskly boiling water-bath and here permitted to remain for exactly one hour. At the end of this time the bottle containing the arsenious acid was removed from the bath, permitted to cool to such a degree that it caused no inconvenience when held in the hand, and then carefully opened. The solution was emptied into a small flask, the bottle well rinsed out with pure water and the entire liquid diluted to 150 cc. After introducing the platinum spiral, boiling down to one-half the original volume, cooling and diluting to 300 cc., the arsenic was determined by titrating with $\frac{1}{40}$ normal iodine in the manner already described.

A.—Using 5 cc. H_2KAsO_4 solution, 20 cc. sulphurous acid, and reducing as above, I obtained:

No.	St. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	5 cc.	15.80 cc.	0.0297 gram.	0.0392 gram.	0.0456 gram.
2	5	15.80	0.0297	0.0392	0.0456
3	5	15.65	0.0294	0.0389	0.0452
4	5	15.75	0.0296	0.0391	0.0455
5	5	15.80	0.0297	0.0392	0.0456
6	5	15.65	0.0294	0.0389	0.0452
7	5	15.80	0.0297	0.0392	0.0456
8	5	15.80	0.0297	0.0392	0.0456
9	5	15.70	0.0295	0.0390	0.0453

5 cc. = 0.0296 gram As = 0.039 gram As_2O_3 = 0.0453 gram As_2O_5.

2. Using 10 cc. HK_2AsO_4 solution, 20 cc. sulphurous acid, and reducing, I obtained:

No.	St. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	10 cc.	31.4 cc.	0.0591 gram.	0.0781 gram.	0.0907 gram.
2	10	31.5	0.0593	0.0783	0.0910
3	10	31.5	0.0593	0.0783	0.0910
4	10	31.45	0.0592	0.0782	0.0908
5	10	31.5	0.0593	0.0783	0.0910
6	10	31.4	0.0591	0.0781	0.0907

10 cc. = 0.0593 gram As = 0.0782 gram As_2O_3 = 0.0907 gram As_2O_5.

3. Using 20 cc. H_2KAsO_4 solution, 30 cc. sulphurous acid, and reducing, I obtained:

No.	St. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	20 cc.	62.5 cc.	0.1177 gram.	0.1556 gram.	0.1805 gram.
2	20	62.7	0.1181	0.1559	0.1811
3	20	62.65	0.1180	0.1557	0.1808

20 cc. = 0.1186 gram As = 0.1564 gram As_2O_3 = 0.1814 gram As_2O_5.

B. To test the method still further, six determinations were made with the solution containing 2.475 gram As_2O_3, as As_2O_5, in a litre. 20 cc. were used in each test, and the reduction was effected in the usual way. I obtained:

No.	St. Solution.	1-40 Normal Iodine.	As.	As_2O_3.	As_2O_5.
1	20 cc.	19.9 cc.	0.0375 gram.	0.0495 gram.	0.0575 gram.
2	20	19.8	0.0373	0.0492	0.0572
3	20	19.8	0.0373	0.0492	0.0572
4	20	19.85	0.0374	0.0493	0.0573
5	20	19.8	0.0373	0.0492	0.0572
6	20	19.8	0.0373	0.0492	0.0572

20 cc. = 0.0375 gram As = 0.0495 gram As_2O_3 = 0.0575 gram As_2O_5.

These figures are a trifle lower than those obtained when the reduction was effected by Holthof's method. 20 cc. of the above solution should require exactly 19.9 cc. $\frac{1}{40}$ normal iodine, whereas the quantity actually used when following Holthof's directions was 20.1 cc. I have already given good reasons for believing that in this case the excess of iodine is due to organic substances which are present in the large quantities of water necessary in making a test in accordance with the first method.

Some time last year we received from a firm in Philadelphia a sample of what purported to be arsenic acid, c. p. A quantitative test proved, however, that it was in nowise chemically pure arsenic acid, but a mixture of arsenious and arsenic acids. The comparatively small precipitate obtained with magnesia mixture indicated clearly that the arsenious acid was the principal constituent. The article is in lumps, some of which, owing to their porcelain-like appearance, are immediately recognised as arsenious acid. I have examined this *so-called* arsenic acid by my modifications of the Reich and Mohr-Holthof methods, and in the following manner: A portion of the material was finely pulverised, 3.0 grams were

carefully weighed out, dissolved in a little warm caustic potash and diluted to a litre. 20 cc. were then brought into a beaker, evaporated to dryness upon the water-bath three times with fuming nitric acid, and the arsenic determined according to my last modification of the Reich process. I obtained 0.0558 gram As_2O_3, which represents the total arsenic calculated to arsenious oxide.

In the following table I give the results of six determinations of the actual amount of As_2O_3 present, each determination being made according to Mohr and with 20 cc. of the original solution:

No.	Solution.	1-40 Normal Iodine.	As_2O_3.
1	20 cc.	18.2 cc.	0.0452 gram.
2	20	18.15	0.0451
3	20	18.2	0.0452
4	20	18.2	0.0452
5	20	18.25	0.0453
6	20	18.15	0.0451

Since 20 cc. = 0.0452 gram, 1000 cc. = 2.260 grams As_2O_3, or 3.0 grams substance = 2.26 grams As_2O_3, which gives 75.33 per cent. As_2O_3.

The table below presents the results of six more determinations, the 20 cc. solution taken being first reduced under pressure with sulphurous acid, then boiled down one-half, and finally titrated:

No.	Solution.	1-40 Normal Iodine.	As_2O_3.
1	20 cc.	22.6 cc.	0.0562 gram.
2	20	22.6	0.0562
3	20	22.4	0.0557
4	20	22.4	0.0557
5	20	22 4	0.0557
6	20	22.4	0.0557

As present as As_2O_3, according to Reich, 0.0558 gram; 0.0557 — 0.0452 = 0.0105 gram arsenious acid present as arsenic acid. Inasmuch as 99 As_2O_3 = 115 As_2O_5, 0.0105 gram As_2O_3 = $\frac{115 \times 0.0105}{99}$ = 0.0122 gram As_2O_5. Since 20 cc. = 0.0122 gram As_2O_5, 1000 cc. = 0.610 gram or 3.0 grams substance = 0.610 gram As_2O_5, which gives 20.33 per cent. As_2O_5. The rest is undoubtedly moisture. A small sample of the substance when heated gently in a glass tube closed at one end gave quite a strong reaction for water.

In closing I would like to say that although the Mohr-Holthof method is most admirably adapted for estimating arsenic in such compounds as soluble salts, yellow and red arsenic glass, and mixtures of arsenious and arsenic oxides, for determining the element in minerals, speisses, mattes and slags, the modified Reich method is, to my mind, much to be preferred. The latter method, though possibly not so *scientifically* perfect as the former, is certainly more rapid, convenient and practical. Above all things it is singularly well suited for determining arsenic in the various kinds of metallurgical products. I have almost finished an exhaustive examination of this method, and I trust erelong to be in the position to describe the results obtained.

JOHN C. GREEN SCHOOL OF SCIENCE, *Princeton, N. J., August* 1, 1885.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.,

Rumford Professor in Harvard University.

(Continued from p. 338.)

ANTIMONOSO-PHOSPHO-TUNGSTATES.

These salts are formed under the same conditions as the corresponding arsenoso-phospho-tungstates, and the methods of analysis to be employed are the same.

22 : 6 : 5 : 12 *Potassic Antimonoso-phospho-tungstate.*—When a solution of potassic phosphate is poured into a hot solution of sodic antimonoso-tungstate as obtained by dissolving SbOCl in 10 : 4 sodic tungstate, a very pale yellow highly crystalline salt is at once formed. This is nearly insoluble in both hot and cold water. The portion analysed was filtered off, washed upon the filter-pump with cold water, drained, and dried upon woollen paper. The salt, like many others which I have described, could not be recrystalised, but I give the results of the analyses for what they may prove to

be worth. They certainly, I think, establish the existence of the series. In this salt,

{ 0.7776 gram gave 0.6142 gram oxides = 78.99 per cent.
{ 0.7776 gram gave 0.4763 gram $PtCl_6K_2$ = 11.90 per cent.

1.0323 gram gave with iodine 0.1594 gram Sb_2O_3 = 15.44 per cent.

0.9716 gram gave with iodine 0.1509 gram Sb_2O_3 = 15.53 per cent.

1.2300 gram gave 0.1805 gram $P_2O_7Mg_2$ = 9.20 per cent. P_2O_5.

1.2430 gram gave 0.1821 gram $P_2O_7Mg_2$ = 9.37 per cent. P_2O_5.

The analyses lead to the formula:

$$22WO_3.5Sb_2O_3.6P_2O_5.12K_2O + 48Aq,$$

which requires

		Calculated.	Found.	
$22WO_3$	5104	54.34	54.23	
$6P_2O_5$	852	9.07	9.20	9.37
$5Sb_2O_3$	1440	15.33	15.44	15.53
$12K_2O$	1133	12.07	11.90	
$48H_2O$	864	9.19	9.13 (diff.)	
	9393	100.00		

ANTIMONIO-TUNGSTATES.

As already stated, these compounds are formed by direct oxidation of antimonoso-tungstates, one molecule of oxygen being absorbed. I shall hereafter show that, in place of oxygen, platinous chloride and other divalent compounds may serve as complex replacing molecules. Antimonio-tungstates are also formed when antimonic hydrate in excess is boiled with an acid tungstate, and when tungstic teroxide is digested or boiled with an alkaline antimonate. The salts of this series are, as a whole, not so well defined as the phospho-tungstates, vanadio-tungstates, and arseniotungstates, and are much more difficult to prepare in a state of purity.

Analytical Methods.—These are essentially the same as those which I have given in the case of the antimonoso-tungstates. Antimonic and tungstic oxides may be precipitated together by mercurous nitrate and mercuric oxide. In the ignited precipitate it must be assumed that the antimony is in the form of tetroxide, Sb_2O_4, and the proper correction applied, after a special determination of the antimony, as sulphide or as metal.

6 : 2 *Antimonio-tungstate of Potassium.*—This salt was prepared by boiling potassic di-antimonate for a long time with a solution of 12 : 5 acid potassic tungstate. After filtration from a small quantity of the antimonate in excess, the filtrate, on standing twenty-four hours, deposited colorless granular crystals, which were washed with cold water and dried upon woollen paper. The salt was not very soluble in water; the crystals were soft and packed together between the fingers. In this salt,

1.0881 gram lost on ignition with WO_4Na_2 0.1076 gram = 9.89 per cent.

1.3566 gram lost on ignition with WO_4Na_2 0.1379 gram = 10.16 per cent.

1.4636 gram gave 1.1178 gram $WO_3 + Sb_2O_4$ = 76.36 per cent.

1.3425 gram gave with KCy 0.2529 gram Sb = 25.12 per cent. Sb_2O_5.

0.9095 gram gave with KCy 0.1700 gram Sb = 24.92 per cent. Sb_2O_5.

0.8710 gram gave 0.5011 gram $PtCl_6K_2$ = 11.16 per cent. K_2O.

The analyses lead to the formula

$$12WO_3.4Sb_2O_5.6K_2O + 25Aq,$$

which requires:

		Calculated.	Found.	
$12WO_3$	2784	54.81	55.04	
$4Sb_2O_5$	1280	25.19	25.12	24.92
$6K_2O$	566	11.14	11.16	
$25H_2O$	450	8.86	8.91	8.64
	5080	100.00		

In calculating the results of the analysis for comparison, I have assumed that, in the ignition with the sodic tungstate to determine the water, antimonic oxide is reduced to the tetroxide Sb_2O_4; a correction must therefore be applied to the apparent loss. This amounts to one-twentieth of the percentage of antimonic pentoxide, and is of course to be deducted from the total loss. Chemists usually admit the existence of three classes of antimonates, corresponding respectively to metaphosphates, pyrophosphates, and orthophosphates, and formulas to support this view have been somewhat arbitrarily assigned to known compounds. If we suppose that the antimonio-tungstate above described contains

metantimonic oxide, we may write the formula as we shall write those of corresponding metaphospho-tungstates,

$$12WO_3.8SbO_3K.2K_2O + 25Aq.$$

A solution of this salt gives white crystalline precipitates with baric chloride, argentic nitrate, and cupric sulphate, and a yellow flocky-crystalline precipitate with mercurous nitrate.

ANTIMONIO-MOLYBDATES.

Salts belonging to this group are formed when freshly prepared antimonic hydrate is boiled with an acid molybdate in solution, when antimonic pentachloride in solution in chlorhydric acid is poured into a solution of an alkaline molybdate in small quantities at a time, and when molybdic oxide is digested with a solution of an alkaline antimonate.

Analytical Methods.—The separation of antimony from molybdenum cannot be effected by sulphydric acid, because molybdic sulphide is always precipitated in greater or less quantity, even when phosphoric acid is present in the solution. The only method which I have been able to devise consists in fusing the salt to be analysed or the mixture of oxides with potassic cyanide, as in the case of the separation of antimony from tungsten. In this case also it is always advisable, and sometimes necessary, to add a sufficient quantity of an alkaline carbonate to form a mixture of neutral molybdate and antimonate, as suggested by Mr. Herman Schmidt. With proper care the two oxides may be precipitated together by mercurous nitrate and mercuric oxide, and ignited without sensible loss of molybdic oxide; but there is then always a certain amount of reduced metallic antimony present, and on the whole the method is not to be recommended.

7 : 4 : 5 *Ammonic Antimonio-molybdate.*—Antimonic hydrate dissolves readily on boiling with a strong solution of 14 : 6 ammonic molybdate. The hydrate should be in excess, and should be added in small portions at a time, until, after long boiling, a part remains undissolved. After standing twenty-four hours, beautiful colorless crystals are deposited in quantity. These have a nacreous lustre, and are readily soluble in hot water. In this salt,

1.0647 gram lost on ignition with WO_4Na_2 0.2052 gram = 19.55 per cent.

1.2234 gram gave 0.2418 gram NH_4Cl = 9.60 per cent. $(NH_4)_2O$.

0.9576 gram gave with KCy 0.3321 gram Sb = 46.24 per cent. Sb_2O_5.

The analyses correspond with the formula

$$7MoO_3.4Sb_2O_5.5(NH_4)_2O + 12Aq,$$

which requires:

		Calculated.	Found.
$7MoO_3$	1008	36.47	36.52
$4Sb_2O_5$	1280	46.31	46.24
$5(NH_4)_2O$	260	9.40	9.60
$12H_2O$	216	7.82	7.64
	2764	100.00	

The formula may also be written

$$7MoO_3.8SbO_3NH_4.(NH_4)_2O + 12Aq.$$

The solution of this salt gives with manganous sulphate after a time a fine canary-yellow crystalline precipitate. The ammonium salt appears to be decomposed by evaporation to dryness, or perhaps by the act of solution. The dry residue, on addition of water, leaves a white insoluble crystalline substance.

The existence of classes of vanadio-phospho-tungstates and vanadio-phospho-molybdates has already been proved. These may be embraced under the general formulas

$$mV_2O_5.nP_2O_5.pWO_3,rR'''_2O \qquad m'V_2O_5.n'P_2O_5.p'MoO_3,rR'''_2O.$$

I believe that I am fully justified, though from qualitative experiments only, in maintaining that the formula

$$mR_2O_5.nR'_2O_5.pR''_2O_3rR'''_2O$$

is general, and that R_2O_5 and R'_2O_5 may represent any two pentoxides, at least of the series $P_2O_5.V_2O_5.As_2O_5$ and Sb_2O_5.

PYROPHOSPHO-TUNGSTATES.

The phospho-tungstates and phospho-molybdates which have hitherto been described must be regarded as containing phosphoric oxide in the modification in which it exists in the class of tribasic or orthophosphates. This appears to be clearly shown, first, by the synthesis of these compounds from orthophosphoric acid and orthophosphates and the acid tungstates and molybdates; and, secondly, from the fact that in all cases, after the addition of an excess of ammonia, magnesia-mixture at once throws down the characteristic ammonio-magnesic orthophosphate. I shall now show that the other modifications of phosphoric oxide or acid

enter as such into similar compounds, so that we have perfectly well defined groups of pyrophospho-tungstates, metaphospho-tungstates, etc., and corresponding compounds containing molybdenum; and that, in the compounds so formed, the various modifications of phosphoric oxide preserve as it were their individuality. I shall further render it at least probable that there are groups—of phospho-tungstates for instance—in which two different modifications of phosphoric oxide may exist, each preserving its own characteristic properties. I do not now assert that in each of the complex groups which I have described orthophosphoric acid may be replaced by some other modification. That remains for experimental investigation. It is at least clear that the field already opened for study is one of practically unlimited extent, as even an elementary application of the algebraical theory of permutations and combinations will show.

Pyrophospho-tungstates are formed when tungstic hydrate or tungstic oxide which has not been ignited is boiled with an alkaline pyrophosphate. The oxide readily dissolves, usually forming a yellow liquid. It is best to employ sodic pyrophosphate, as this gives a much more soluble salt, but the pyrophosphate must be specially prepared in the laboratory, and the tungstic oxide should be in excess. Neutral salts of the heavy metals usually give precipitates in solutions of the alkaline pyrophospho-tungstates; these precipitates are not necessarily salts of the same group, but are very often at least either pyrophosphates of the metallic bases or double pyrophosphates of the metal and of sodium or potassium.

Analytical Methods.—These are the same as those which I have employed in the case of the orthophospho-tungstates, only in the determination of the phosphoric oxide it is necessary to evaporate the salt two or three times in succession to dryness with an excess of chlorhydric acid, so as to convert the phosphoric acid present completely into the ortho or tribasic form. In the absence of any standard of comparison, it is necessary to speak with much hesitation, but it has always appeared to me that in these salts—in other words, in the presence of tungstic oxide—the conversion of pyrophosphoric acid into orthophosphoric acid is more difficult, or at least takes place more slowly, than in the case of the ordinary pyrophosphates. Tungstic and phosphoric oxides may in these compounds also be precipitated together by mercurous nitrate and mercuric oxide.

22 : 3 : 6 *Ammonio-sodic Pyrophospho-tungstate.*—A boiling solution of sodic pyrophosphate readily dissolves tungstic oxide as prepared by the action of chlorhydric or nitric acid upon calcic tungstate, but not ignited. The filtrate has a dull yellow color, and gives with a strong solution of ammonic chloride an abundant white crystalline precipitate, which cannot be purified by recrystallisation, but which may be well washed upon the filter-pump with cold water, in which it is soluble to a very small extent. Hot water in large excess dissolves it, but even cold ammonia water dissolves it with much difficulty. When boiled for a long time with a solution of mercurous nitrate, the salt gives at first a white and finally a yellow mercurous salt. Argentic nitrate in solution gives at first with the salt extremely minute talcose scales, but on boiling for some time the whole dissolves to a clear liquid. When the salt is boiled with a solution of baric chloride, a flocky-crystalline white baric salt is formed. Cupric sulphate on boiling dissolves the pyrophospho-tungstate, but on cooling a pale green crystalline body separates, which does not contain tungsten. The salt, precipitated by ammonic chloride as above, after washing with cold water and drying upon woollen paper, was analysed:

0.6626 gram lost on ignition 0.1060 gram = 16.00 NH_3 and H_2O.

0.9866 gram gave 0.2479 gram $P_2O_7Mg_2$ = 16.07 per cent. P_2O_5.

0.5488 gram gave 0.0499 gram $(NH_4)_2O$ = 9.09 per cent.

0.8188 gram gave 0.6504 gram oxides = 79.46 per cent. WO_3 and P_2O_5.

In determining the phosphoric oxide, the salt was several times in succession evaporated to dryness with nitric acid.

The analyses agree with the formula

$$22WO_3.3[P_2O_7Na_4]6[P_2O_7(NH_4)_4]2(NH_4)_2O + 31Aq,$$

which requires:

		Calculated.	Found.
$22WO_3$	5104	63.48	63.39
$9P_2O_5$	1278	15.90	16.07
$6Na_2O$	372	4.63	4.54 (diff.)
$14(NH_4)_2O$	728	9.06	9.09
$31H_2O$	558	6.93	6.91
	8040	100.00	

As already stated, the salt is dissolved by a large excess of hot water to a clear colorless solution. Cupric sulphate gives in this solution a pale blue crystalline precipitate of a pyrophosphate free from tungstic oxide. Argentic nitrate and baric chloride give white flocky-crystalline precipitates. Either, therefore, the salt is decomposed by solution or by the action of cupric sulphate.

22 : 9 : 18 *Potassic Pyrophospho-tungstate.* — When potassic bromide and acetic acid are added to the saturated solution of tungstic oxide in sodic pyrophosphate, a white granular fine-grained crystalline precipitate very slightly soluble in cold water is formed at once. For analysis the salt was washed upon the filter-pump with cold water, and dried on woollen paper. In this salt,

0.9440 gram gave 0.6717 gram oxides = 71.15 per cent. WO_3 and P_2O_5.

1.3647 gram gave 0.9721 gram oxides = 71.23 per cent. WO_3 and P_2O_5.

0.9070 gram gave 0.2015 gram $P_2O_7Mg_2$ = 14.21 per cent. P_2O_5.

0.9817 gram lost 0.0960 gram H_2O = 9.78 per cent.

The phosphoric oxide was determined as before by evaporation with nitric acid to convert the pyrophosphoric into orthophosphoric acid.

The analyses correspond to the formula

$$22WO_3.9P_2O_7K_4 + 49Aq,$$

which requires:

		Calculated.	Found.	
$22WO_3$	5104	56.94	56.94	57.02
$9P_2O_5$	1278	14.26	14.21	
$18K_2O$	1699	18.96	19.07	
$49H_2O$	882	9.84	9.78	
	8963	100.00		

22 : 9 : 13 *Potassic Pyrophospho-tungstate.* — This salt was obtained by boiling tungstic oxide for some time with potassic pyrophosphate. After filtration and standing a white crystalline salt separated, which was well drained on the filter-pump, and then washed with cold water in which it is but slightly soluble. In much boiling water it dissolves on boiling to a clear liquid. The solution gives a white crystalline precipitate with argentic

nitrate—no precipitate at first with cupric sulphate. On boiling, a very pale blue crystalline salt separates, which does not contain tungsten, and is either a cupric pyrophosphate or a double salt of potassium and copper. The solution of the pyrophospho-tungstate gives a dense white distinctly crystalline precipitate with mercurous nitrate, and a turbid solution with baric chloride yielding on boiling a white feathery crystalline salt. No precipitate is formed with manganous sulphate, but after a short time the solution becomes turbid. In this salt,

1.6112 gram gave 1.2119 gram oxides = 75.22 per cent.

1.9796 gram gave 1.4894 gram oxides = 75.23 per cent.

1.6421 gram gave 0.3862 gram $P_2O_7Mg_2$ = 15.06 per cent.

1.2433 gram lost by direct ignition 0.1299 gram = 10.45 per cent.

The analyses agree closely with the formula

$$22WO_3.6P_2O_7K_4.3P_2O_7H_4.K_2O.H_2O + 42Aq,$$

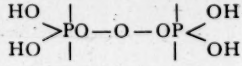
so that the type is, as in other cases,

$$22WO_3.9P_2O_7H_4.2R_2O.$$

The formula requires:

		Calculated.	Found.	
$22WO_3$	5104	60.11	60.17	60.18
$9P_2O_5$	1278	15.05	15.05	
$13K_2O$	1227	14.45	14.32 (diff.)	
$49H_2O$	882	10.39	10.45	
	8491	100.00		

All the compounds of this group which I have obtained belong, as will be seen, to the same type which contains the frequently recurring chemical mass of twenty-two molecules of tungstic oxide, united to nine molecules of pyrophosphoric acid or a pyrophosphate, together with a certain amount of base over and above that required to saturate the phosphoric oxide. We may represent this group provisionally by a structural formula containing *nine* groups of the form:



Further investigation will doubtless show that there are other series of pyrophospho-tungstates and analogous pyrophospho-

molybdates. It is especially desirable to study the compounds which remain in solution after the precipitation of part of the pyrophosphoric oxide by means of cupric sulphate.

It may here be remarked, that Wallroth[1] has described a series of pyrophosphates which contain *nine* molecules of P_2O_7, united in each case to thirty-six atoms of metal. Thus we have

$$Ca_{10}Na_{16}(P_2O_7)_9$$
$$Mg_{10}Na_{16}(P_2O_7)_9$$
$$Co_{10}Na_{16}(P_2O_7)_9$$
$$Ni_{10}Na_{16}(P_2O_7)_9.$$

It would therefore appear that similar complex molecules enter directly into combination with twenty-two molecules of tungstic oxide, but that the complexity is not necessarily due to a determining action on the part of the latter.

MONOMETAPHOSPHO-TUNGSTATES.

In preparing the salts of this series I have employed ordinary glacial phosphoric acid, which, according to Brescius,[2] contains about 50 per cent. of sodic metaphosphate, and which may be regarded as a mixture of sodic metaphosphate and metaphosphoric acid. I have assumed that the acid is here in the form of monometaphosphoric acid, although upon this point the evidence is still insufficient. As the relations of metaphosphoric acid to indicators of various kinds have not hitherto been studied, the following brief note may be of interest. A solution of glacial phosphoric acid is neutral to tropæolin. The same solution required for equal volumes with purpurin 23 cc. sodic hydrate solution; with hæmatoxylin, 14 cc.; and with alizarin, 12.5 cc. No definite end reaction could be obtained with phenol-phthalein, methyl-orange or rosolic acid.

Monometaphospho-tungstates are formed by the direct action of the acid upon acid tungstates. They are, frequently at least, gummy uncrystalline bodies. When crystalline the crystals are usually soft, and pack together readily. The salts of the alkaline earths are usually more or less distinctly crystalline. Those of the heavy metallic oxides are often pasty, and sometimes oily. They are not very readily converted into orthophospho-tungstates, and in this respect they seem to differ materially from the corresponding metaphospho-molybdates.

[1] Bull. de la Soc. Chimique [2], **39**, 316. [2] Zeitschrift für analytische Chemie **6**, 187.

Analytical Methods.—In these salts tungstic and metaphosphoric oxides may be precipitated together by mercurous nitrate and mercuric oxide. Metaphosphoric acid may be converted into orthophosphoric acid by dissolving the salt in the least possible quantity of water, adding strong sulphuric acid, evaporating the solution nearly to dryness, and repeating this process several times. This method is very much better than fusion with alkaline carbonates, which effects the transformation of metaphosphoric acid in a very imperfect manner. I believe that I can assert with entire confidence, that in the class of monometaphospho-tungstates the conversion of the metaphosphoric into orthophosphoric acid is much more difficult than in the metaphosphates. The precipitation of the orthophosphoric acid by magnesia mixture must of course be repeated twice.

24:2:3 *Potassic Monometaphospho-tungstate.*—When a cold freshly prepared solution of glacial phosphoric acid is digested with 10:4 potassic tungstate, part of this salt dissolves, while the undissolved portion changes its character, and is converted into a soft crystalline, very slightly soluble mass. This may be filtered off and washed with cold water. In this salt,

1.5236 gram lost on ignition 0.0857 gram = 5.63 per cent. H_2O.
1.5236 gram gave 0.0517 gram $P_2O_7Mg_2$ = 1.96 per cent. P_2O_5.
0.9934 gram gave 0.0303 gram $P_2O_7Mg_2$ = 2.17 per cent. P_2O_5.
1.0686 gram gave 0.0352 gram $P_2O_7Mg_2$ = 2.11 per cent. P_2O_5.
1.1490 gram gave 1.0171 gram oxides = 88.52 per cent.
1.1490 gram gave 0.3327 gram $PtCl_6K_2$ = 5.70 K_2O.

The anlyses correspond very well to the formula

$$24WO_3.2[PO_2K]3K_2O + 20Aq,$$

which requires:

		Calculated.		Found.	
$24WO_3$	5568	86.36		86.38	
P_2O_5	142	2.21	2.11	2.17	1.96
$4K_2O$	376	5.84		5.70	5.85 (diff.)
$20H_2O$	360	5.59		5.63	
	6446	100.00			

The filtrate from the 24:2 salt, on standing, deposits a white crystalline salt, which, when thrown on a filter and washed with cold water, presents a colorless gummy mass. Of this salt,

0.6183 gram gave 0.0307 gram $P_2O_7Mg_2$ = 3.17 per cent. P_2O_5.

{ 0.8173 gram gave 0.6844 gram oxides = 83.72 per cent.
{ 0.8173 gram lost on ignition 0.0607 gram = 7.43 per cent.

From an oversight, the potassic oxide was not determined in this salt, which may be either

$$16WO_3.2[PO_3K]2K_2O.2Na_2O + 20Aq,$$

or

$$16WO_3.2[PO_3K]5Na_2O + 20Aq.$$

The formulas require, respectively,

		Calc'd.		Found.	Calc'd.			
$16WO_3$	3712	80.34		80.56	80.38		3712	$16WO_3$
P_2O_5	142	3.07		3.17	3.07		142	P_2O_5
$3K_2O$	283	6.12	8.80	8.87	2.04	8.76	94	K_2O
$2Na_2O$	124	2.68			6.72		310	$5Na_2O$
$20H_2O$	360	7.79		7.40	7.79		360	$20H_2O$
	4621	100.00			100.00		4618	

18 : 1 : 2 *Ammonic Monometaphospho-tungstate.*—When 12 : 5 ammonic tungstate is boiled with a solution of glacial phosphoric acid, a white crystalline mass remains undissolved, very different in appearance from the ammonic tungstate employed. This salt requires a large quantity of boiling water for solution, but is only slightly soluble in cold water. For analysis, it was thoroughly drained upon the filter-pump, and then washed with cold water. Of this salt,

1.6896 gram lost by ignition with WO_4Na_2 0.1082 gram = 6.40 per cent.

1.5026 gram gave 0.0745 gram $P_2O_7Mg_2$ = 3.17 per cent. P_2O_5.

1.4267 gram gave 0.0316 gram $(NH_4)_2O$ = 2.21 per cent.

The analyses correspond to the formula

$$18WO_3.2[PO_3NH_4].(NH_4)_2O + 11Aq,$$

which requires:

		Calculated.	Found.
$18WO_3$	4176	90.39	90.43
P_2O_5	142	3.08	3.17
$2(NH_4)_2O$	104	2.25	2.21
$11H_2O$	198	4.28	4.19
	4620	100.00	

The filtrate from this salt gives on evaporation a thick colorless syrup, in which white crystals—perhaps of the salt above described—were suspended. It will be seen that the action of PO_3H upon 12 : 5 ammonic tungstate is essentially the same as upon the 10 : 4 potassic salt, and that in each case at least one crystalline and one gummy salt are formed.

The analyses given are sufficient to establish the existence of three classes of monometaphospho-tungstates. My work on this subject is to be regarded merely as preliminary, and is intended to direct the attention of other chemists to this class of salts. In another paper I shall give the results of a more detailed study of the various metaphospho-tungstates. Fleitmann and Henneberg have described five series of metaphosphates; in addition to these, there remain to be studied, in their relation to tungstic and molybdic oxides, the two series of tetraphosphates, $P_4O_{11}.6RO$ and dekaphosphates, $P_{10}O_{19}.12RO$, discovered by the same chemists, as well as the new group of salts described by Salzer,[1] which may be called hypophosphates.

ORTHOMETAPHOSPHO-TUNGSTATES.

A single salt of this series will be sufficient to establish the existence of compounds into which two different modifications of phosphoric acid enter, to a certain extent at least preserving their peculiar characteristics.

22 : 6 : 11 : 7 *Potassio-sodic Orthometaphospho-tungstate.*—When 24 : 1 sodic phospho-tungstate is boiled with a solution of sodic monometaphosphate, PO_3Na, the salt dissolves readily to a clear liquid. Potassic bromide gives a white precipitate in this solution. After filtering and washing with cold water, a white gelatinous mass remains upon the filter, but slightly soluble in water. Of this salt,

1.2008 gram gave 0.8728 gram oxides = 72.68 per cent.

1.5959 gram gave 0.1611 gram oxides = 72.76 per cent.

1.3558 gram gave 0.2220 gram $P_2O_7Mg_2$ = 10.47 per cent. P_2O_5.

0.8822 gram gave 0.5774 gram $PtCl_6K_2$ = 12.70 per cent. K_2O.

1.4517 gram lost on ignition with WO_4Na_2 0.1349 gram = 9.29 per cent.

The analyses correspond with the formula

$$22WO_3.6P_2O_5.11K_2O.7Na_2O + 42Aq,$$

[1] Pharmaceutische Zeitung, Bunzlau, 1881. Ann. der Chemie, **211**, 1.

which requires:

		Calculated.	Found.
$22WO_3$	5104	62.36	62.25
$6P_2O_5$	852	10.41	10.47
$11K_2O$	1038	12.68	12.70
$7Na_2O$	434	5.31	5.29
$42H_2O$	756	9.24	9.29
	8184	100.00	

The solution of this salt in chlorhydric acid gives, with magnesia-mixture and ammonia, a precipitate which appears to contain ammonio-magnesic phosphate and magnesic metaphosphate. It is of course possible that a portion of the metaphosphoric acid may have been converted into orthophosphoric acid by the act of solution in chlorhydric acid. I know of no method by which really reliable determinations, either qualitative or quantitative, can be made in compounds of this kind. In the analysis above, the salt was evaporated several times with strong sulphuric acid, and the phosphoric acid then determined with magnesia-mixture. The total quantity of base in the salt is exactly sufficient to saturate six molecules of orthophosphoric acid, but the salt certainly contains at least a part of the phosphorus as metaphosphoric oxide. We may perhaps assume that the two modifications are equally divided between the bases, and the formula may be then written

$$22WO_3.3(P_2O_5.3K_2O).6PO_3Na.2K_2O.4Na_2O + 42Aq.$$

The subject of course requires further investigation.

MONOMETAPHOSPHO-MOLYBDATES.

The salts belonging to this series appear also to belong to two different classes, which may be simply distinguished as crystalline and gummy salts. Both these classes are readily converted by acids into orthophospho-molybdates. Up to the present time I have made only a preliminary study of these compounds.

10 : 2 : 5 *Ammonic Monometaphospho-molybdate.*—When glacial phosphoric acid is neutralised with ammonia, and the solution is mixed with one of 14 : 6 ammonic molybdate, no precipitate is formed, but on evaporation a thick, nearly colorless gummy mass is formed. On standing for some time, this is almost completely converted into a crystalline mass. This may be drained, redis-

solved in water, in which it is very soluble, and recrystallised several times from very concentrated solutions. It then presents very beautiful, perfectly colorless, flat tabular crystals. The solution gives at once, with nitric acid, a precipitate of yellow orthophospho-molybdate; with magnesia-mixture and ammonia, a precipitate very different from ammonio-magnesic orthophosphate. Argentic nitrate gives a flocky-crystalline precipitate; baric and thallous nitrates give beautiful white feathery-crystalline salts; mercurous nitrate gives a pale flocky-crystalline precipitate, while cuprous sulphate forms none. Of this salt,

1.4314 gram gave 0.3002 gram $P_2O_7Mg_2$ = 13.41 per cent. P_2O_5

0.8385 gram gave 0.1022 gram $(NH_4)_2O$ = 12.19 per cent.

1.4016 gram lost 0.2776 gram = 19.81 per cent.

The analyses agree with the formula

$$10MoO_3.2P_2O_5.5(NH_4)_2O + 9Aq,$$

which requires:

		Calculated.		Found.	
$10MoO_3$	1440	67.10	80.33	66.78	80.19
$2P_2O_5$	284	13.23		13.41	
$5(NH_4)_2O$	260	12.12		12.19	
$9H_2O$	162	7.55		7.62	
	2146	100.00			

The formula may be more advantageously written

$$10MoO_3.4[PO_2NH_4).3(NH_4)_2O + 9Aq.$$

Empirically, this salt has, except as regards water of crystallisation, the same formula as the acid 10 : 2 orthophospho-molybdate, which I have already described.

HEXAMETAPHOSPHO-MOLYBDATES.

The single salt of this series which I have thus far obtained will serve as an example, and I hope as an incentive to further study.

14 : 3 : 4 *Baric Hexametaphospho-molybdate.*—Sodic hexametaphosphate, obtained by heating the so-called microcosmic salt until a clear colorless glass is obtained, gives a white colorless crystalline salt with baric chloride, which, after washing with cold water, readily dissolves in an excess of a solution of 14 : 6 ammonic

molybdate. After a short time the clear filtered solution deposits an abundance of beautiful colorless acicular crystals. This salt cannot be perfectly decomposed by boiling with a solution of mercurous nitrate. Nitric acid dissolves it to a turbid liquid, with formation of a yellow powder. After boiling with the acid, ammonic molybdate gives the characteristic yellow crystalline precipitate, indicating the presence of orthophosphoric acid. Of this salt,

1.0140 gram lost on ignition with WO_4Na_2 0.2463 gram = 24.31 per cent.

1.8970 gram gave 0.4286 gram SO_4Ba = 14.84 per cent. BaO.

2.0403 grams gave 0.3454 gram $P_2O_7Mg_2$ = 10.83 per cent. P_2O_5.

The formula appears to be

$$14MoO_3.3P_2O_5,4BaO + 55Aq,$$

which requires:

		Calculated.	Found.
$14MoO_3$	2016	49.86	50.02
$3P_2O_5$	426	10.53	10.83
$4BaO$	612	15.13	14.84
$55H_2O$	990	24.48	24.31
	4044	100.00	

I give this formula with much reserve, and only as probably correct. To express the presence of hexametaphosphoric oxide it may be written

$$14MoO_3.[Ba_3.6PO_3].BaO + 55Aq.$$

I shall return to the subject at another time.

STANNO-PHOSPHO-TUNGSTATES.

The vanadico-vanadio-tungstates and vanadico-vanadio-molybdates which I have described furnish instances of compounds embraced under the general formulas

$$mRO_3.nR'O_2.pR''_2O_5.rR'''_2O.$$

I shall show that the compounds belonging to this type are very numerous, and frequently very well defined. For the present, it will be sufficient to cite two new series of hitherto undescribed salts, my object being to direct the attention of other chemists to a

new field of investigation, and to point out methods of preparation and of analysis which may facilitate their work.

Stanno-phospho-tungstates are formed when the stanno-chlorides of ammonium or of the alkaline metals are mixed in solution with acid alkaline phospho-tungstates. They are colorless crystalline salts, so far as studied. As a representative of this series we may take the ammonium salt.

Analytical Methods.—In these salts the three higher oxides may be determined together by precipitation with mercurous nitrate and mercuric oxide, but the ignited oxides should be evaporated once or twice with nitric acid to oxidize any reduced tin. Tin may be separated as metal by fusion with potassic cyanide, and phosphoric oxide may be determined after separating tin with sulphydric acid.

22 : 2 : 1 : 2 *Ammonic Stanno-phospho-tungstate.*—When a solution of stanno-chloride of ammonium is poured into a clear cold solution of 24 : 1 sodic phospho-tungstate ($24WO_3.P_2O_5.2Na_2O + 27Aq$), a beautiful white crystalline precipitate is formed at once. This is but slightly soluble in boiling water. By long boiling with baric chloride, argentic nitrate, or mercurous nitrate, the salt gives crystalline compounds, which in the cases of the barium and silver salts are colorless; in that of the mercurous salt, yellow. So far as can be determined without quantitative analyses, there appears to be in these cases only a simple double decomposition. For analysis the ammonium salt was thoroughly washed with cold water on the filter-pump, drained, and dried on woollen paper. Of this salt,

1.3577 gram lost on ignition with WO_4Na_2 0.0833 gram = 6.14 per cent.

1.2921 gram lost on ignition without WO_4Na_2 0.0811 gram = 6.29 per cent.

1.6822 gram gave 0.0646 gram Sn = 4.88 per cent. SnO_2.

1.1596 gram gave 1,0850 gram oxides = 93.57 per cent.

1.1826 gram gave 0.0443 gram $P_2O_7Mg_2$ = 2.39 per cent.

0.9575 gram gave 0.0182 gram $(NH_4)_2O$ = 1.89 per cent.

The analyses correspond well with the formula

$$22WO_3.2SnO_2.P_2O_5.2(NH_4)_2O + 15Aq,$$

which requires:

$22WO_3$	5104	86.21	86.30
$2SnO_2$	300	5.06	4.88
P_2O_5	142	2.39	2.39
$2(NH_4)_2O$	104	1.75	1.89
$15H_2O$	270	4.59	4.24
	5920	100.00	99.70

STANNO-PHOSPHO-MOLYBDATES.

The salts of this series are formed under precisely the same conditions as the corresponding stanno-phospho-tungstates. It is at least probable that it will be found that the two classes of salts may be formed under other conditions, as, for example, by boiling stannic oxide with phospho-tungstates and phospho-molybdates, or by digesting stanno-tungstates and stanno-molybdates with alkaline phosphates or with phosphoric acid; but I have made no experiments to determine these points.

Analytical Methods.—Tin may be determined in these salts by fusion with potassic cyanide, provided that, as in the case of the separation of antimony from tungsten and from molybdenum, a sufficient quantity of an alkaline carbonate is added to convert all the higher oxides present into neutral salts. Under these circumstances, no insoluble compound of molybdenum is formed, and the tin separates in bright metallic globules. Phosphoric acid may be determined in these salts after separating the whole of the tin and the greater part of the molybdenum by means of sulphydric acid. Molybdic oxide is estimated most advantageously by difference.

16:4:3:3 *Ammonic-Stanno-phospho-molybdate.*—When a solution of stanno-chloride of ammonium, $SnCl_4(NH_4)_2$, is poured into a hot solution of acid ammonic phospho-molybdate.

$$10MoO_3.2P_2O_5.5(NH_4)_2O + 7Aq,$$

a fine bright yellow crystalline precipitate is formed, which quickly settles and leaves a colorless solution. The salt is almost insoluble, even in boiling water, and may perhaps find an application in the separation and quantitative estimation of tin. On boiling with mercurous nitrate it gives a buff-yellow crystalline mercurous salt. Under the same circumstances cupric sulphate yields yellowish-

green crystals, and argentic nitrate a very pale yellow, not distinctly crystalline salt. An excess of ammonia readily decomposes the salt with separation of a white gelatinous mass. Of this salt,

0.8648 gram gave 0.1023 gram metallic tin = 15.18 per cent. SnO_2.

2.3780 grams gave 0.3865 gram $P_2O_7Mg_2$ = 10.40 per cent. P_2O_5.

1.2021 gram gave 0.2016 gram $P_2O_7Mg_2$ = 10.73 per cent. P_2O_5.

1.0130 gram gave 0.3839 gram $(NH_4)_2O$ = 3.79 per cent.

1.7170 gram lost on ignition 0.2793 gram = 16.27 per cent.

The analyses give the formula

$$16MoO_3 . 4SnO_2 . 3P_2O_5 . 3(NH_4)_2 + 28Aq,$$

which requires

		Calculated.	Found.	
$16MoO_3$	2304	57.75	57.97	(diff.)
$4SnO_2$	600	15.04	15.19	
$3P_2O_5$	426	10.67	10.73	10.40
$3(NH_4)_2O$	156	3.91	3.79	
$28H_2O$	504	12.63	12.48	
	3990	100.00		

ALUMINO-MOLYBDATES.

Heinrich Struve,[1] in 1854, described a remarkable series of salts, which he regarded simply as double molybdates of the sesquioxides of aluminum, iron, manganese, chromium, and ammonia, potash, or soda. These salts were embraced under two different types, particular aluminic, ferric, and chromic salts, having respectively the formulas

$$Al_2O_3.6MoO_3 + 3(K_2O.2MoO_3) + 20Aq.$$
$$Fe_2O_3.6MoO_3 + 3(K_2O.2MoO_3) + 20Aq.$$
$$Cr_2O_3.6MoO_3 + 3(Na_2O.2MoO_3) + 21Aq.$$

The manganic salt, on the other hand, was represented by

$$Mn_2O_3.6Mo_3 + 5(K_2O.2MoO_3) + 12Aq.$$

Parmentier[2] has recently added a new term to this series, the type being

$$R_2O_3.10MoO_3.2R'_2O + xAq.$$

[1] Petersburg Acad. Bull., **12**, 142. [2] Comptes Rendus, **95**, 839.

The true character of these compounds could not be understood at the time of their discovery. I find that in solutions of the salts described by Struve, potassium or ammonium may be directly replaced by other metals or by alkaloids,—a fact which was, however, noticed by Struve himself. In addition,—and this is of more importance,—I find that there are series which contain the sesquioxides named with phosphoric and molybdic oxides, so that we have classes of ferro-phospho-molybdates, etc. From my point of view, the compounds in question may be classed under three types, of which the following will serve as representatives:

Alumino-dodeka-molybdates, $Al_2O_3.12MoO_3.6R_2O$.

Ferrico-dodeka-molybdates, $Fe_2O_3.12MoO_3.6R_2O$.

Chromico-dodeka-molybdates, $Cr_2O_3.12MoO_3.6R_2O$.

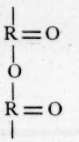
Manganico-hekkaideka-molybdates, $Mn_2O_3.16MoO_3.5K_2O.H_2O + 11Aq$.

Alumino-deka-molybdates, $Al_2O_3.10MoO_3.2R_2O$.

Ferrico-deka-molybdates, $Fe_2O_3.10MoO_3.2R_2O$.

Chromico-deka-molybdates, $Cr_2O_3.10MoO_3.2R_2O$.

All these classes of salts containing oxides corresponding to chlorides of the type R_2Cl_6 are very much less stable than compounds containing oxides of the types R_2O_5, RO_2, and R_2O_3 (corresponding to chlorides RCl_5). We may assume provisionally that the component



enters into the structural formulas which represent this class of compounds. Struve states that he has obtained similar compounds containing tungsten, but these have not been described.

Klein[1] has carefully studied four series of boro-tungstates, embraced respectively under the general formulas

$$7WO_3.B_2O_3.2R_2O$$
$$9WO_3.B_2O_3.2R_2O$$
$$12WO_3.B_2O_3.4R_2O$$
$$14WO_3.B_2O_3.3R_2O.$$

[1] Bull. de la Société Chim. [2,] **36**, 547, **37**, 202.

Since boron is the lowest term in the third column of the periodic series, aluminum being the next higher, it would seem probable that the oxides which correspond to still higher terms in the same column will form similar compounds. Chromium, manganese, iron, nickel, and cobalt may be regarded as higher harmonics of aluminum, and at least three of these form analogous series. It still remains to study the relations of the oxides of the cerium and yttrium groups to molybdic and tungstic oxides, since these correspond to chlorides of the type RCl_3, and yet differ in a very marked degree from oxides like As_2O_3, Sb_2O_3, etc. I have made some progress in this investigation and will in another paper give my results in detail.

GENERAL CONCLUSIONS.

The formulas and details which I have given in the present instalment of my work appear to justify the following general conclusions.

1. Vanadic pentoxide unites with phosphoric or arsenic pentoxides in various proportions to form well-defined complex acids. In some, at least, of these, we seem to have series in which vanadic pentoxide plays the same part as tungstic or molybdic teroxide, or, in other words, appears to enter the compound as $V_2O_3.O_3$.

2. Compounds of vanadic pentoxide, vanadic dioxide, and phosphoric or arsenic pentoxide, may be formed, possessing properties analogous to those of the compounds of tungstic or molybdic teroxides with pentoxides and dioxides.

3. The series of oxides P_2O_3, As_2O_3, Sb_2O_3, unite with tungstic and molybdic oxide to form well-defined series of complex acids. In these the ratio of the number of molecules of the oxides of the types R_2O_3 and MO_3 is much lower than in the cases of the compounds which contain orthophosphoric or ortho-arsenic acids.

4. Compounds exist which contain one oxide of the R_2O_3 (or RO_3H_3) and one of the type R'_2O_5 united to tungstic or molybdic oxide, the general formula being

$$mMO_3 . nR_2O_3 . pR'_2O_5 . rR''_2O .$$

5. Compounds exist which contain acids of the types RO_2H_3 (hypo-phosphorous acid, for instance) and R'_2O_5 united to tungstic or molybdic oxides, the general formula being

$$mMO_3 . nRO_2H_3 . pR'_2O_5 . rR''_2O .$$

6. Classes of compounds exist which contain oxides of the types RO_3 and R'_2O_5 united to tungstic or molybdic oxides, the general formula being

$$mMO_3.nRO_3.pR'_2O_5.rR_2O,$$

where, as in the other general formulas, M represents either tungsten or molybdenum.

7. Compounds exist which contain pyrophosphoric and metaphosphoric acids in place of orthophosphoric acid. So far as it is possible to judge from the salts analysed, these contain, or at least may contain, phosphoric and tungstic or molybdic oxides in a lower ratio to each other than in the ortho-phospho-compounds.

8. Complex acids exist which contain two different modifications of phosphoric acid, as, for instance, metaphosphoric and orthophosphoric acids or oxides.

9. The salts described by Struve and by Parmentier establish the existence of a class of complex acids, which contain oxides of the type R_2O_3, corresponding to chlorides of the type R_2Cl_6. The true character of these salts is for the first time recognized.

Partly for convenience of reference, and partly to show as distinctly as possible the extent and richness of the field of investigation now opened, I have collected all the formulas of the last and present instalments of my work, prefixing the mark † to those which are in my judgment less certainly established.

Phospho-vanadates.

$P_2O_5.V_2O_5.(NH_4)_2O + Aq.$
$P_2O_5.V_2O_5.2Ag_2O + 5Aq.$
$P_2O_5.2V_2O_5.(NH_4)_2O + 7Aq.$
$4\,P_2O_5.6V_2O_5.3K_2O + 21Aq.$
$7\,P_2O_5.6V_2O_5.3H_2O + 34Aq.$
$20\,V_2O_5.P_2O_5.3H_2O + 56Aq.$

Arsenio-vanadates.

$5As_2O_5.8V_2O_5.3H_2O + 24Aq.$
† $7As_2O_5.6V_2O_5.3H_2O.$

Phospho-vanadico-vanadates.

$18V_2O_5.VO_2.2P_2O_5.7(NH_4)_2O + 50Aq.$
† $4V_2O_5.VO_2.5P_2O_5.4Na_2O + 37Aq.$
$12P_2O_5.12VO_2.6V_2O_5.5K_2O + 40Aq.$
$12P_2O_5.14VO_2.6V_2O_5.7K_2O + 52Aq.$
$14P_2O_5.16VO_2.6V_2O_5.7(NH_4)_2O + 67Aq.$
$10P_2O_5.11VO_2.5V_2O_5.5(NH_4)_2O + 41Aq.$

Arsenio-vanadico-vanadates.

$12As_2O_5.12VO_2.6V_2O_5.5(NH_4)_2O + 7Aq.$
$9As_2O_5.9VO_2.8V_2O_5.4(NH_4)_2O + 11Aq.$

Vanadico-vanadates.

$4V_2O_5.2VO_2.(NH_4)_2O + 8Aq.$

Hypophospho-molybdates.

$8MoO_3.2PO_2H_3.2(NH_4)_2O + 2H_2O.$

Hypophospho-tungstates.

$18WO_3.6PO_2H_3.4K_2O + 7Aq.$

Phosphoroso-molybdates.

$24MoO_3.4PO_3H_3.4(NH_4)_2O + 17Aq.$
$24MoO_3.4PO_3H_3.4(NH_4)_2O + 25Aq.$

Phosphoroso-tungstates.

$22WO_3.4PO_3H_3.6(NH_4)_2O + 25Aq.$
$32WO_3.16PO_3H_3.5K_2O + 46Aq.$
$22WO_3.8PO_3H_3.2Na_2O + 25Aq.$

Arsenoso-tungstates.

$18WO_3.2As_2O_3.7(NH_4)_2O + 18Aq.$
$18WO_3.2As_2O_3.8BaO + 42Aq.$
$16WO_3.8As_2O_3.9Na_2O + 65\ Aq.$

Arsenoso-molybdates.

$8MoO_3.2As_2O_3.3BaO + 13Aq.$
†$12MoO_3.5As_2O_3(NH_4)_2O + 24Aq.$
$6MoO_3.3As_2O_3.2MnO + 6Aq.$

Antimonoso-tungstates.

$11WO_3.3Sb_2O_3.2BaO + 18Aq.$

Antimonoso-molybdates.

$17MoO_3.3Sb_2O_3.6(NH_4)_2O + 21Aq.$

Phosphoroso-phospho-tungstates.

$24WO_3.P_2O_5.2PO_3H_3.5K_2O + 13Aq.$

Phosphoroso-phospho-molybdates.

$72MoO_3.3P_2O_5.2PO_3H_3.9(NH_4)_2O + 38Aq.$

Phospho-hypophospho-tungstates.

$26WO_3.4P_2O_5.2PO_3H_3.9K_2O.Na_2O + 43Aq.$

Arsenoso-phospho-tungstates.

$32WO_3.14As_2O_3.3P_2O_5.10K_2O + 28Aq.$
$12WO_3.2As_2O_3.2P_2O_5.5K_2O.Na_2O + 15Aq.$
$60WO_3.As_2O_3.4P_2O_5.7K_2O + 55Aq.$

Arsenoso-arsenio-tungstates.

$\dagger 21WO_3.As_2O_3.4As_2O_5.10K_2O + 26Aq.$

Antimonoso-phospho-tungstates.

$22WO_3.5Sb_2O_3.6P_2O_5.12KO + 48Aq.$

Vanadio-molybdates.

$6MoO_3.V_2O_5.2(NH_4)_2O + 5Aq.$
$16MoO_3.2V_2O_5.5BaO + 29Aq.$
$18MoO_3.V_2O_5.8(NH_4)_2O + 15Aq.$

Vanadio-tungstates.

$5WO_3.V_2O_5.4(NH_4)_2O + 13Aq.$
$10WO_3.V_2O_5.6H_2O + 16Aq.$
$18WO_3.V_2O_5.6H_2O + 30Aq.$

Antimonio-tungstates.

$12WO_3.4Sb_2O_5.6K_2O + 25Aq.$

Antimonio-molybdates.

$7MoO_3.4Sb_2O_5.5(NH_4)_2O + 12Aq.$

Pyrophospho-tungstates.

$22WO_3.9P_2O_5.6Na_2O.14(NH_4)_2O + 31Aq.$
$22WO_3.9P_2O_5.18K_2O + 49Aq.$
$22WO_3.9P_2O_5.13K_2O + 49Aq.$

Monometaphospho-tungstates.

$\dagger 16WO_3.2[PO_3K]5Na_2O + 20Aq.$
$24WO_3.2[PO_3K]3K_2O + 20Aq.$
$18WO_3.2[PO_3NH_4](NH_4)_2O + Aq.$

Monometaphospho-tungstates.

$10MoO_3.44[PO_3NH_4].3(NH_4)_2O + 9Aq.$

Hexametaphospho-molybdates.

† $14MoO_3.[Ba_3.6PO_3].BaO + 55Aq.$

Orthometaphospho-tungstates.

$22WO_3.3[P_2O_5.3K_2O][6PO_3Na].2K_2O.2Na_2O + 42Aq.$

Phospho-vanadio-molybdates.

$48MoO_3.2P_2O_5.V_2O_5.7(NH_4)_2O + 30Aq.$
$14MoO_3.P_2O_5.8V_2O_5.8(NH_4)_2O + 50Aq.$

Phospho-vanadio-tungstates.

$60WO_3.3P_2O_5.V_2O_5.10(NH_4)_2O + 60Aq.$
$16WO_3.P_2O_5.3V_2O_5.5(NH_4)_2O + 37Aq.$
$60WO_3.3P_2O_5.2V_2O_5.18BaO + 144Aq.$
$18WO_3.3P_2O_5.4V_2O_5.8K_2O + 32Aq.$
† $7WO_3.P_2O_5.V_2O_5.3K_2O + 11Aq.$

Vanadico-vanadio-molybdates.

$28MoO_3.VO_2.4V_2O_5.11(NH_4)_2O + 20Aq.$
$30MoO_3.3VO_2.2V_2O_5.14BaO + 48Aq.$

Vanadico-vanadio-tungstates.

$12WO_3.3VO_2.2V_2O_5.6Na_2O + 43Aq.$
$12WO_3.3VO_2.2V_2O_5.6(NH_4)_2O + 12Aq.$
$12WO_3.3VO_2.2V_2.2V_2O_5.6Ag_2O + 8Aq.$

Stanno-phospho-molybdates.

$16MoO_3.4SnO_2.3P_2O_5.3(NH_4)_2O + 28Aq.$

Stanno-phospho-tungstates.

$22WO_3.2SnO_2.P_2O_52(NH_4)_2O + 15Aq.$

Phospho-vanadio-vanadico-tungstates.

$60WO_3.3P_2O_5.V_2O_5VO_2.18BaO + 15Aq.$

To these I will add the new formulas of the salts described by Struve and Parmentier:

Struve's Salts.

$Al_2O_3.12MO_3.6KO + 20Aq.$
$Al_2O_3.12MoO_3.6(NH_4)_2O + 20Aq.$
$Al_2O_3.12MoO_3.6Na_2O + 22Aq.$[1]
$Fe_2O_3.12MoO_3.6K_2O + 20Aq.$
$Fe_2O_3.12MoO_3.6(NH_4)_2O + 20Aq.$
$Cr_2O_3.12MoO_3.6K_2O + 20Aq.$
$Cr_2O_3.12MoO_3.6(NH_4)_2O + 20Aq.$
$Cr_2O_3.12MoO_3.6Na_2O + 21Aq.$
$Mn_2O_3.16MoO_3.5K_2O + 21Aq.$
$Mn_2O_3.16MoO_3.5(NH_4)_2O + 12Aq.$

Parmentier's Salts.

$Al_2O_3.10MoO_3.2K_2O + 15Aq.$
$Fe_2O_3.10MoO_3.2K_2O + 15Aq.?$
$Cr_2O_3.10MoO_3.2K_2O + 15Aq.?$

[*To be continued.*]

Contributions from the Chemical Laboratory U. S. Department of Agriculture.

V.—ON THE ESTIMATION OF ACETIC ACID IN LIQUIDS CONTAINING ORGANIC MATTER, BY DISTILLATION.

By H. W. Wiley.

Having had occasion to make an examination of some samples of kumys, I was led to enquire whether any other acid except lactic was present. The microscope showed the presence of bacteria aceti, and thus established the presence of acetic acid.

In a substance so complex as kumys the estimation of a minute quantity of acetic acid is a matter of great difficulty. In order to accomplish it in at least an approximate manner I determined to

[1] Gentele, Journal für prakt. Chemie, **81**, 413.

try the method of Duclaux[1] which rests upon the assumption that acetic acid in a solution subjected to distillation gives a definite percentage of its weight in given successive portions of the distillate. When ten-elevenths of the original liquid has been distilled the portion of the acid given off amounts to 79.8 per cent.

Mr. A. H. Allen[2] who quotes M. Duclaux' results states that in the only trial he has made of the method, viz.: the estimation of the acid in acetate of lime the quantity obtained was considerably below the amount claimed by M. Duclaux.

This fact caused me to suppose that the actual percentage of acid distilled depended largely on the percentage present as well as on the total amount of the distillate. In order to submit this idea to the test of experiment I made a large number of distillations of pure fresh milk to which varying amounts of acetic acid of known strength were added.

I found that in order to have a liquid residue of 10 to 15 cc. left in the retort when 100 cc. of milk were used and the distillate equalled 100 cc. in volume it was necessary to add to the milk the dilute acid and enough water to bring the total volume up to 130 cc. After numerous trials I find that at least 15 cc. of liquid residue should remain in the retort at the end in order to prevent the casein, sugar, etc., from burning.

The quantity of liquid remaining in the retort was determined by pouring the whole of the residue in a linen filter and measuring the volume of the filtrate. In the following experiments the residual liquid varied between 14 and 16 cc. in quantity. A solution of fifth normal acetic acid was used of which 1 cc. contained .012 gram of pure acid.

Since the amount of acetic acid in sour milk or kumys can never be very great in quantity the trials were made with very weak solutions.

The quantities of fifth normal acid used varied from 5 to 30 cc. in a volume of 130 cc. A large number of distillations were made in various attempts to prevent the frothing of the acidulated milk and the consequent transfer of portions of it to the distillate. The best methods of preventing frothing will be given hereafter.

Method Employed.

In each case 100 cc. of milk were used. To this the acetic acid solution was added and then enough water to make the volume

[1] Ann. Chem. et Phys. (5) Vol. XI, p. 233 *et seq.*

[2] Com. Organic Analysis, 2d edition, Vol. I. p. 408 *et seq.*

up to 130 cc.. Each 10 cc. of the distillate was titrated separately by $\frac{N}{100}$ soda, using phenolphtalein as indicator.

Results with 5 *cc.* $\frac{N}{5}$ $HC_2H_3O_2$.

Percentage acid present by weight .044. The mean of a large number of distillations showed that the total acid distilled in 100 cc. when the above amount was present was only 7.33 per cent. of the whole. The quantity given off in each 10 cc. of distillate as well as the total is given below:

1.	10 cc. of distillate,	.33 per cent.
2.	10 "	.33– .66
3.	10 "	.39–1.05
4.	10 "	.35–1.40
5.	10 "	.40–1.80
6.	10 "	.59–2.39
7.	10 "	.60–2.99
8.	10 "	.90–3.89
9.	10 "	1.25–5.14
10.	10 "	2.19–7.33

It may be doubted whether it is worth while to try to estimate so minute a portion of acid as .044 per cent., but even this amount can be detected as a trace in a mixture of it with lactic acid, when the latter does not exceed .30 per cent., as will be shown subsequently.

Results with 10 *cc.* $\frac{N}{5}$ $HC_2H_3O_2$.

10 cc. fifth normal acetic acid contain .12 gram anhydrous acid. In 135 grams this is .089 per cent.

The amount of total acid present coming over with each successive portion of 10 cc. distillate was as follows (mean of 100 tirations):

1.	10 cc.	.89 per cent.
2.	10	1.12– 1.91
3.	10	1.27– 3.18
4.	10	1.31– 4.49
5.	10	1.42– 5.91
6.	10	1.59– 7.50
7.	10	1.87– 9.37
8.	10	2.20–11.57
9.	10	2.69–14.26
10.	10	3.75–18.01

Results with 15 *cc.* $\frac{N}{5}$ $HC_2H_3O_2$.

Following are the mean result of 120 titrations.

Percentage Present.

Fifteen cubic centimetres of fifth normal acetic acid represent a weight of pure acid of .18 gram. In 135 of grams of material this represents .133 per cent.

The mean percentages of total acid present coming over with each successive 10 cc. of distillate were as follows:

1.	10 cc. of distillate.	1.02 per cent.
2.	10 "	1.19– 2.21
3.	10 "	1.28– 3.49
4.	10 "	1.42– 4.91
5.	10 "	1.63– 6.54
6.	10 "	1.97– 8.51
7.	10 "	2.32–10.83
8.	10 "	2.76–13.59
9.	10 "	3.44–17.03
10.	10 "	4.55–21.58

Results with 20 *cc.* $HC_2H_3O_2$.

20 cc. of fifth normal acetic acid have .24 gram of water free acid. In 135 grams of material this amounts to .178 per cent.

In all 260 titrations were made.

Following are the mean results showing percentage of total acid present, coming over in each successive 10 cc. of distillate.

1.	10 cc	1.30 per cent.
2.	10	1.56– 2.86
3.	10	1.78– 4.64
4.	10	1.88– 6.52
5.	10	2.15– 8.67
6.	10	2.50–11.17
7.	10	2.90–14.07
8.	10	3.48–17.55
9.	10	4.23–21.78
10.	10	5.58–27.26

Results with 30 *cc.* $HC_2H_3O_2$.

30 cc. $\frac{N}{5}$ $HC_2H_3O_2$ contain .36 gram anhydrous acid.
In 135 grams of material this is .267 per cent.

The percentage of acid coming over with each successive 10 cc. distillate was as follows (mean of 120 determinations):

1.	10 cc.	1.80 per cent.
2.	10	1.92– 3.72
3.	10	2.00– 5.72
4.	10	2.13– 7.85
5.	10	2.40–10.25
6.	10	2.75–13.00
7.	10	3.03–16.03
8.	10	3.92–19.75
9.	10	4.80–23.95
10.	10	6.13–30.08

It was reasonable to suppose that an organic acid like lactic acid would itself be carried over mechanically to a certain extent in the process of distillation. Since pure acetic acid boils first when the temperature reaches 119°, all that comes over of it also must be carried mechanically in the other vapors, or as a definite hydrate of low boiling point. To determine how much of the lactic acid would thus pass over, a large number of trials were made. 20 cc. $\frac{N}{5}$ lactic acid in a total weight of 135 grams were used in these determinations. The amount that came over in each successive portion of 10 cc. of distillate was almost constant, and did not rapidly increase toward the last, as is always the case with acetic acid. The mean for each 10 cc. was .0064 cc. of the acid employed, or .0016 per cent. For the whole distillate of 100 cc. this would give .016 per cent. of the acid present. The percentage of lactic acid in the mixture distilled was .27. It is fair to presume that with a larger quantity of lactic acid the amount carried over mechanically must be somewhat greater.

In any case, however, with small percentage of lactic acid, the disturbing effect of the quantity going over can be approximately determined, and in no case is it very great.

It appears, therefore, that in a total acidity (in kumys or sour milk) of from .50 to 1.00 per cent. due to the two acids, viz. lactic and acetic, it is possible to determine each of them with a satisfac-

tory degree of accuracy, when the quantity of acetic acid present does not rise above .3 or fall below .1 per cent. If it should be less than .1 per cent. the quantities distilled become so minute that the results are not reliable.

It would be interesting to continue the investigations with larger quantities of both acids, but since they do not usually occur in kumys or sour milk in greater amounts, the operations should be conducted in a liquid of a less complex nature than milk.

Separation of the Two Acids in Artificial Mixtures.

To test the accuracy of the determinations I had my assistant, Mr. Dugan, prepare for me various mixtures of milk and the two acids in proportions unknown to me. In most instances I was able to determine with gratifying accuracy the quantities used. In a few cases, however, the results were not accurate, but these were chiefly due to the use of a smaller quantity of the acids than indicated in the limits stated above, for the accuracy of the method.

Following are some of the results of the separation. The quantities of acid employed as well as of those found by analysis are given in cubic centimetres of fifth normal acid :

Trial No. 1.

Found	...	10.6	cc. acetic acid.
Given	...	10.0	" "
Found	...	00.0	" lactic acid.
Given	...	2.5	" "

Trial No. 2.

Found	...	.92	cc. acetic acid.
Given	...	1.00	" "
Found	...	8.78	" lactic acid.
Given	...	9.00	" "

Trial No. 3.

Found	...	.67	cc. acetic acid.
Given	...	.50	" "
Found	...	8.42	" lactic acid.
Given	...	9.50	" "

Trial No. 4.

Found	...	2.94 cc. acetic acid.
Given	...	3.50 " "
Found	...	6.29 " lactic acid.
Given	...	6.50 " "

Retention of a Portion of the Acid by the Precipitated Casein.

As I have already mentioned, I find that the best method of clarifying the milk for determining total acid present is by mixing it with an equal volume of strong alcohol. I found, however, using known quantities of acid in the milk, in titrating the filtrate, that the total acidity was not indicated. Here are some of the numbers obtained—in parts of acid known to have been added to the milk:

1	94.40 per cent.	(lactic and acetic.)
2	98.04 "	" "
3	86.67 "	(lactic acid alone.)
4	96.20 "	(acetic " ")

It would appear from the above numbers that lactic acid is held back with more tenacity than acetic. As will be seen the error which may occur from the above cause is likely to be greater than that arising from the distillation.

The exact cause of the error, its extent and its remedy are subjects for future study.

As a result of the work the following method of procedure may be recommended:

1. The sample of sour milk is mixed with an equal volume of alcohol, the acid determined in the filtrate with $\frac{N}{5}$ NaOH, using phenolphtalein as indicator. The quantity found to be taken at 95 per cent. of the amount present.

2. 100 cc. of the sour milk are diluted to 130 cc. with water and a distillate of 100 cc. taken off. The acetic acid in this distillate is estimated (using $\frac{N}{50}$ or $\frac{N}{100}$ alkali if necessary).

If less than 12 cc. $\frac{N}{100}$ NaOH are required to neutralise the acid in the distillate, it can be assumed that not more than 10 per cent. of the acetic acid present has been distilled over. From the total acidity, however, must first be deducted that due to the lactic acid carried over mechanically. If .3 per cent. lactic acid be present it will be proper to deduct 6 cc. $\frac{N}{100}$ from the total used.

If 40 cc. $\frac{N}{100}$ be required under the conditions above noted then 18 per cent. of the acetic acid may be considered to have come over. If 70 cc. $\frac{N}{100}$ NaOH be required the acid distilled over should be estimated at 23 per cent.

If 110 $\frac{N}{100}$ NaOH be required, place the amount of acid distilled over at 27 per cent.

If the distillate require 200 cc. $\frac{N}{100}$ NaOH the quantity of acid distilled over can be taken at 31 per cent.

For quantities intermediate among those given allow for proportionate percentages in the distillate.

Frothing of the Sample during Distillation.

Whether the object of distillation be the estimation of acid or alcohol the difficulty of preventing frothing of the sample is great. I found that an ordinary test-tube brush placed in the neck of the flask was a most excellent safety plug. The handle of the brush should be cut off so as not to interfere with the stopper. A thread tied to the stump of the handle and left hanging outside does not interfere with the stopper and is convenient for withdrawing the brush. The brush should be at first pushed into the flask and then by means of the thread pulled up into the throat. The bristles then all point downward in a convenient position to puncture the bubbles. For alcohol distillations nothing better than this need be used. In the case of acids, however, there may be some danger of the metal of the brush being attacked, and some other device must be used. I found a small fine sponge pulled into the throat of the flask by a thread very efficient means of arresting the bubbles. Another excellent device is the use of a plug of fine asbestos fibre or of glass wool. In all these cases the amount of liquid which the plugs will absorb must be approximately known and this additional quantity of water added to the contents of the flask. I also employed a small platinum cylinder punctured with fine holes which was attached by a rubber stopper to the delivery tube. The simplest device of all is to use a flask with a side delivery tube. The neck of the flask should be largest at the top and have a small constriction just as it enters the bulb. A perforated platinum cone large enough to fill the neck is placed point down in it. The constriction prevents it from entering the bulb. In this way the bubbles are prevented from entering the delivery tube and no correction is to be made for absorbed liquids.

VI.—AN EXAMINATION OF WHISKIES.

By Clifford Richardson.

As far as I have been able to learn very few careful examinations of American whiskies are a matter of record. During the past year several samples have come into my hands from reputable retail and wholesale dealers and from bonded warehouses through the United States Commissioner of Internal Revenue. Determinations have been made in these samples of alcohol and solid residue, for the purpose of learning what was to be expected in whiskies of different ages and blendings.

It is well known that a new whiskey contains practically no solids in solution. The amount found after a short time in bonded warehouse is derived from the extractive matter of the wood of the barrels in which the liquor is stored. As the whiskey ages the amount of solid matter it contains increases, both from additional solution and evaporation, or by some of the aging processes which heat the liquor and enable it to dissolve more substances from the staves. After a certain age the "straight whiskies" from the warehouse, on which taxes have been paid, are blended and treated to suit the market. Very few straight whiskies are sold as such in America, it having been found desirable from a commercial point of view to mix the product of different fermentations or mashes which have a different flavor, to add artificial flavoring material, such as tea and spices and sugar, and often to reduce the strength with water.

This is a matter purely of taste. From an analytical point of view, to the food analyst it is of interest to know the limits within which these operations affect the character of a whiskey as manipulated by the best dealers.

The following samples have been examined:

Retail Trade.—3681, Cutter whiskey, eight year old Bourbon, Ky.; 3682, Private Stock, seven year old rye, Pa.; 3683, Loyal Legion, five years old rye, Md.; 3684, Gibson, five year old rye, Pa.; 3685, Orator, five year old rye, Pa.; 3686, Webster, five year old rye; 3687, Cutter D No. 1 five year old rye, Ky.; 3688, XXXX Gibson, four year old rye, Pa.; 3689, Old Crow, five year old Bourbon, Ky.; 3690, Cutter R. R., three year old rye, Ky.; 3691, Hammond, five year old rye, Ohio; 3692, O. K., four year

old rye, Ky.; 3693, Stag Head, three year old rye, Ohio; 3694, Potomac, low grog shop; 3695, Orator "D," six year old rye, Pa.; 3696, Orator Cabinet, ? rye, Pa.

From Bonded Warehouse.—1881–9, six samples of different lots about six months old; 1880–2, three lots of whiskey from Boone Co., Ky., in warehouse but a few months and aged by a patent process; 3853, Aug. 26, 1885, whiskey from bonded warehouses six months old and dark colored, suspected of being tampered with. 4128, November 26th, 1885 Whiskey, one month old, on sale in Kansas, aged by patent process, Boone County, Mo. The following determinations were made:

EXAMINATION OF WHISKEYS.

Retail and wholesale trade.

No.	Specific Gravity Original Whiskey.	Specific Gravity of Distillate 15° C.	Per cent. of Alcohol.	Total solids per 100.	Ash.
3681	.93692	.93259	43.5	1.0290	.0078
3682	.93662	.93544	42.2	.7176	.0098
3683	.93646	.93396	42.9	.9170	.0060
3684	.93683	.93555	42.1	.5540	.0085
3685	.93470	.93392	42.9	.6168	.0099
3686	.93601	.93488	42.4	.7690	.0110
3687	.93436	.93366	43.0	.5858	.0030
3688	.93602	.93483	42.4	.5902	.0100
3689	.94411	.93835	40.7	1.4520	.0085
3690	.93422	.93335	43.2	.4760	.0039
3691	.93092	.93087	44.4	.1240	.0029
3692	.92894	.92887	45.3	.1500	.0048
3693	.94105	.93746	41.2	.9664	.0039
3694	.95993	.93786	41.0	.2060	.0047
3695	.93650	.93335	43.2	.6964	.0090
3696	.95685	.93445	42.1	.5386	.0078
Average	.93878		42.7	.6493	.0069

Bonded warehouses.

1881	.93418	...	42.8	.0304	...
1882	.93428	...	42.7	.0346	...
1883	.93410	...	42.8	.0304	...
1884	.93337	...	43.2	.0364	...
1885	.93359	...	43.1	.0248	...
1886	.93340	...	43.2	.0396	...
1887	.93292	...	43.4	.0392	...
1889	.93263	...	43.0	.0344	...
Average	.93368	...	43.0	.0337	...

Bonded warehouse; aged by patent process.

No.	Specific Gravity Original Whiskey.	Specific Gravity of Distillate 15° C.	Per cent. of Alcohol.	Total solids per 100.	Ash.
1890	.93502	...	42.4	.0672	...
1891	.93465	...	42.5	.0872	...
1892	.93576	...	42.3	.0500	...
4128	.93620	...	41.6	.0738	.0037
Average	.93841	...	42.4	.0695	...

Bonded warehouse.

3853	.93161	...	44.0	.0616	.0036

The results show at once that a straight whiskey six months old averages only .0337 of solids, while at 4 or 5 years they will not exceed .200, as is shown by the straight whiskies numbered 3691 and 3692. The remaining articles in the retail trade all contain an excess of solids which have evidently been added as flavor. The aging processes, so called, apparently add not nearly so much extractive matter to the liquor as one might expect and in no way conceals the true character, although perhaps volatilising a little alcohol and rendering it weaker. In the 29 samples examined the percentage of alcohol varied within rather narrow limits, but one having above 44 per cent., three above 43 per cent., and but three below 42 per cent., twenty-two contain from 42 to 43 per cent. of alcohol by weight, and as the "Proof Spirit" of the United States contains 42.7 per cent. by weight of alcohol, the samples all varied very little from proof.

It will be seen that the evidence of these determinations is sufficient, at least to show whether a whiskey is a straight article or has been flavored.

WASHINGTON, D. C., *November 26th*, 1885.

NOTES.

On "Explosive Ice."

During the very cold weather of the week January 8th to 15th, a French "*gazogène*" or portable apparatus for preparing carbonic-acid water under pressure was destroyed in the laboratory of the University of Virginia, by the freezing of the contents of the upper globe, which was almost completely full of distilled water charged with carbonic acid, and was burst by the expansion of the ice formed. The globe, which was surrounded by basket-work of split cane, was of heavy glass, about 8 mm. in thickness, and must have burst with some violence, judging from the distance to which the disc-like top was thrown. Having removed the apparatus to a warm room, in which thawing might take place without the liquid running about on the shelves and floor of the apparatus room, I had my attention attracted in a few minutes by little crackling explosions coming from the ice, which, when brought in, was quite solid and dry—much below the melting-point. Standing near and somewhat above the level of the apparatus, which had been placed in one of the laboratory sinks, I was two or three times struck in the face by little bits of ice as large as hazel-nuts, thrown off with some force from the bulk of the frozen mass. One piece, fully as large as a walnut, was thrown off to a distance of seven or eight feet upon the floor. Some of the crackling sounds fairly merited the name of explosions. Once or twice the sound was quite as loud as that produced by suddenly treading upon a friction-match.

The ice was in the main white and translucent, but with many small, glassy streaks of complete transparency running through it. It obviously contained a multitude of pretty uniformly distributed, minute bubbles of carbon-dioxide gas under heavy pressure—pressure not due merely to the space within which the gas had been originally generated, but greatly increased by the expansion of the water in the act of freezing as the gas separated out from it. It is, perhaps, not impossible that, at the existing temperature, this pressure may have even sufficed to liquefy some of the gas of the bubbles caught in the interior of the ice. The immediate cause of the explosive splitting up of the ice under the tension of the included carbon dioxide seemed to be the weakening of the forms by expansion in the comparatively warm atmosphere of the room: there was but little melting during the time; some three-quarters of an hour, during which the crackling sounds and the flying to pieces of the ice lasted. A little explosion could easily be induced by striking a very slight blow with a little blowpipe hammer, or with a chisel or other sharp-pointed tool, on almost any part of the ice which had not

before been so treated, and on breaking off some large pieces of the ice and placing them on the table, detached from the rest of the mass, they continued to split and fly to pieces in a very remarkable way.

The whole of the phenomena reproduced exactly the behavior of the quartz from Branchville in Connecticut, in which occur numerous microscopic cavities containing partly liquefied carbon dioxide; but in the case now described, the explosive splitting up by heating was produced at a much lower point on the thermometric scale.

J. W. MALLET.

UNIVERSITY OF VIRGINIA, *January* 18, 1886.

A Gas-Absorption and Measuring Tube.

The accompanying figure, which requires little explanation, represents a form of nitrometer and gas-absorption apparatus that I have found convenient. The measuring tube is graduated in both directions from the stop-cock in cubic centimetres and fractions. The pressure tube is adapted by a ground-joint, and both pressure tube and measuring tube are correspondingly graduated in millimetres. The divisions and their numbers being the same, when the apparatus stands on a level surface the use of a cathetometer is unnecessary.

The stop-cock may be three-wayed, as in Lunge's nitrometer, and the gas can then be transferred to another similar tube when incompatible absorbents are to be employed.

WM. H. GREENE, M. D.

CENTRAL HIGH SCHOOL, *Philadelphia, Nov.* 15, 1885.

Wöhler Monument.

A committee has recently been organised in this country for the purpose of securing subscriptions to the Wöhler-monument fund. According to the last report from Germany, the fund had reached the sum of about $4000. Much more is needed. The chemists of America owe more to Wöhler than to any other one man, and it is hoped that a generous response will be made to the circular which has been sent out by the committee.

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I.—AMERICAN.

BAYLEY, T. The Assay and Analysis of Iron and Steel, Ores and Fuel. New York: Spon. 91 pp. 8vo.

BLYTHE, A. W. Poisons: Their Effects and Detection. Vol. I. New York: Wood. 6 + 98 pp. 8vo.

BOLTON, H. C. A Catalogue of Chemical Periodicals. New York. 58 pp. 8vo.

CHITTENDEN, R. H. Studies from the Laboratory of Physiological Chemistry, Sheffield Scientific School of Yale College. New Haven: Tuttle, Morehouse & Taylor. 4 + 198 pp. 8vo.

CLOWES, F. A Manual of Practical Chemistry. Philadelphia: Lea Brothers. 14 + 376 pp. 8vo.

SCOTT-WHITE, A. H. Chemical Analysis for Schools and Science Classes. New York: Scribner & Welford. 8 + 130 pp. 16mo.

SHOEMAKER, J. F. The Oleates: An Investigation into Their Nature and Action. Philadelphia: Davis. 6 + 121 pp. 16mo.

STAMMER, K. Chemical Problems. Translated from the German by W. S. Hoskinson. Philadelphia: Blakiston. 111 pp. 12mo.

STODDARD, J. T. Outline of Lecture Notes on General Chemistry: The Metals. Boston: Harris, Rogers & Co. 4 + 131 pp. 16mo.

TROILIUS, M. Notes on the Chemistry of Iron. New York: Wiley. 6 + 98 pp. 8vo.

WILLIAMS, W. M. The Chemistry of Cookery. New York: Appleton. 8 + 328 pp. 12mo.

II.—ENGLISH.

ACETIC Acid and Vinegar, Ammonia and Alum. London: Churchill. 200 pp. 8vo.

BRIANT, L. Laboratory Textbook for Brewers. London: Briant. 324 pp. 8vo.

CARNELLEY, T. Melting and Boiling-Point Tables. Vol. I. London: Harrison & Sons. + 352 pp. 4vo.

ELLIS, G. E. R. Practical Organic Analysis. London: Longmans, Green & Co. 8 + 72 pp. 16mo.

HUSBAND, H. A. Aids to the Analysis of Foods and Drugs. London: Baillière. 78 pp. 12mo.

LIVEING, G. D. Chemical Equilibrium the Result of the Dissipation of Energy. London: Bell. 12mo.

—FRENCH.

BERTHELOT. Les Origines de l'Alchimie. Gr. in-8 illustré.

DOCUMENTS sur les falsifications des matières alimentaires et sur les travaux du laboratoire municipal. Deuxième rapport. In-4.

DURAND-CLAYE, C. L. Chimie appliquée à l'art de l'ingenieur. In-8.

FREMY ET TERREIL. Le guide du chimiste. In-8.

GIRARD, AIMÉ. Composition chimique et valeur alimentaires des diverses parties du grain de froment. Avec 3 planches. In-8.

GRIVEAUX, F. Traité de chimie à l'usage des élèves des lycées et collèges de jeunes filles et des candidats au brevet supérieur. Avec 168 fig. In-12.

JOLY, A. Éléments de Chimie rédigés conformément aux programmes officiels du 22 janvier 1885 pour les classes de réthorique et de philosophie. Avec 154 figures. In-12.

JUNGFLEISCH, ÉMILE. Manipulations de chimie. Guide pour les travaux pratiques de chimie de l'École supérieure de pharmacie de Paris. Avec 372 figures. Gr. in-8.

MERMET, A. Manipulations de chimie. Métalloïdes. Avec 228 fig. In-12.

SWARTS, TH. Principes fondamentaux de chimie à l'usage des écoles. Avec 146 figures. Gr. in-8.

WURTZ, AD. Introduction à l'étude de la chimie. Avec 60 figures.

IV.—ITALIAN.

MUSAIO, G. Nozioni elementari di analisi chimica qualitativa delle sostanze minerali. 8vo.

V.—GERMAN.

ARNOLD, C. Repetitorium der Chemie. Mit besonderer Berücksichtigung der für die Medizin wichtigen Verbindungen, sowie der "Pharmacopoea germanica," namentlich zum Gebrauche für Mediziner und Pharmaceuten. 8. Hamburg. 527 pp.

BAUMANN, A. Tafeln zur Gasometrie. Zum Gebrauch in chemischen und physikalischen Laboratorien, sowie an hygienischen Instituten. 8. München. 201 pp.

BEILSTEIN, F. Handbuch der organischen Chemie. 2. gänzlich umgearbeitete Auflage. 1. Lieferung. gr. 8. Hamburg. 80 pp.

BIECHELE, M. Die chemischen Gleichungen der wichtigsten anorganischen und organischen Stoffe. Mit besonderer Berücksichtigung der deutschen und österreichischen Pharmacopoe, sowie der massanalytischen Untersuchungen der Arzneistoffe. Nach den neuesten chemischen Anschauungen bearbeitet. 1. Hälfte. gr. 8. Eichstätt. 404 pp.

CLASSEN, A. Quantitative chemische Analyse durch Elektrolyse. Nach eigenen Methoden. 2. gänzlich umgearbeitete und vermehrte Auflage. Mit 41 Holzschnitten und 1 lithographirten Tafel. 8. Berlin. 189 pp.

FISCHER, B. Lehrbuch der Chemie für Pharmaceuten. Mit besonderer Berücksichtigung der Vorbereitung zum Gehülfen-Examen. I. Hälfte Mit 20 in den Text gedruckten Holzschnitten. gr. 8. Stuttgart. 324 pp.

GEPPERT, J. Die Gasanalyse und ihre physiologische Anwendung nach verbesserten Methoden. Mit 1 lithographirten Tafel und 13 Holzschnitten gr. 8. Berlin. 136 pp.

GUMPRECHT, O. Wie studirt man Chemie und die beschreibenden Naturwissenschaften? Mit Berücksichtigung der sächsischen, preussischen und bairischen Prüfungsordnungen. 8. Leipzig. 30 pp,

HAGER, H. Chemische Reactionen zum Nachweise des Terpentinöls in den ätherischen Oelen, in Balsamen, etc. Für Chemiker, Apotheker, Drogisten und Fabrikanten ätherischer Oele. 8. Berlin. 168 pp.

HAUSHOFER, K. Mikroskopische Reactionen. Eine Anleitung zur Erkennung verschiedener Elemente und Verbindungen unter dem Mikroskop, als Supplement zu den Methoden der qualitativen Analyse. Mit 137 eingedruckten Illustrationen. gr. 8. Braunschweig. 169 pp.

JAHRESBERICHT über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften. Unter Mitwirkung von A. Bornträger, A. Elsas, E. Erdmann, C. Hell, etc., herausgegeben von F. Fittica. Für 1883. 1 Heft. gr. 8. Giessen. 480 pp.

JAHRESBERICHT über die Leistungen der chemischen Technologie mit besonderer Berücksichtigung der Gewerbestatistik für das Jahr 1884. Jahrgang I–XXV bearbeitet von R. v. Wagner. Fortgesetzt von F. Fischer. XXX oder Neue Folge XV Jahrgang.

LANGER, C. UND MEYER, V. Pyrochemische Untersuchungen. Mit 17 in den Text eingedruckten Holzstichen. gr. 8. Braunschweig. 81 pp.

METZGER, S. Pyridin, Chinolin und deren Derivate. Gekrönte Preisschrift der philosophischen Fakultät der Universität Würzburg. gr. 8. Braunschweig. 93 pp.

SCHAEDLER, C. Die Technologie der Fette und Oele der Fossilien (Mineralöle) sowie die Harzöle und Schmiermittel. Mit zahlreichen Text-Illustrationen und mehreren Tafeln. (In ungefähr 7 Lieferungen.) 1. Lieferung. gr. 8. Leipzig. 160 pp.

——Kurzer Abriss der Chemie der Kohlenwasserstoffe. Zugleich ein Repetitorium für Studirende und practische Chemiker, Techniker, Apotheker u. s. w. gr. 8. Leipzig. 202 pp.

WINKLER, C. Lehrbuch der technischen Gasanalyse. Kurzgefasste Anleitung zur Handhabung gasanalytischer Methoden von bewährter Brauchbarkeit. Auf Grund eigener Erfahrung bearbeitet. Mit vielen in den Text eingedruckten Holzschnitten. gr. 8. Freiberg. 132 pp.

F. W. C.

ERRATA.

Page 349 (Vol. 7, No. 5). Fourth line in paragraph 1. *For* 'is found' *read* 'is not found'; and after filtrate *for* the rest of the paragraph *read* 'for the central part of the exceedingly minute grains even of the ore is still magnetic; it has escaped oxidation, and, in consequence of this, it retains some vanadium.'

Page 353. Fourth line in paragraph 19. *For* 'if there is a remnant' *read* 'with the remnant.'